

Podovik, A.N.

✓ New method of synthesis of esters of phosphoric and
thiophosphoric acids. XXI. Addition of alkyl thiophos-
phates and dialkyl dithiophosphoric acids to anils. A. N.
Podovik and M. K. Sergeeva (State Univ., Kazan). *Zh. Obshch. Khim.* 25, 1769-69 (1955); *cf. C.A.* 47, 2687a;

50, 4808c.—An equimolar mixt. of $(RO)_2PSH$ and the de-
sired anil in a small vol. of EtOH was treated with a few
drops of RONA soln.; almost no heat effect was observed.
After 20-30 min. on a steam bath the mixt. was allowed to
solidify. In reactions with $(RO)_2PS_2H$, this was added drop-
wise to an equimolar amt. of anil in EtOH with ice cooling
and the mixt. was finally heated 10-15 min. on a steam bath.
The following $RNHCH(R')P(S)(OR)_2$ were prepd. (R, R',
R¹, % yield, and m.p. given): *p*-MeOC₆H₄, Ph, Et, 43.2,
48°, Ph, *p*-MeNC₆H₄, Et, 60, 100-100.5°, *p*-MeC₆H₄, Ph,
Et, 62.3, 67°, *m*-MeC₆H₄, Ph, Et, 62.2, 77-8°, *m*-MeC₆H₄,
m-MeC₆H₄, Et, 50, 84-5°, 1-C₆H₅, Ph, Et, 64.1, 136.5°,
Ph, Ph, Bu, 78.3, 63°, *p*-MeOC₆H₄, Ph, Bu, 63.2, 45-6°,
Ph, *p*-MeNC₆H₄, Bu, 81.2, 80°, *m*-MeC₆H₄, *m*-MeC₆H₄, 73,
57-8°, Ph, *p*-MeC₆H₄, Bu, 61.3, 36°, *p*-MeC₆H₄, Ph, Bu,
71.8, 75.5°, and *m*-MeC₆H₄, Ph, Bu, 65.6, 47-7.5°. The
following $RNHCH(R')SP(S)(OR)_2$ were prepd. from $(RO)_2$ -
PS₂H (const. as above): Ph, Ph, Et, 69.1, 103-4°, *p*-Me-
C₆H₄, Ph, Et, 60.4, 101-2°, *m*-MeC₆H₄, *p*-MeNC₆H₄, Et,
93.6, 128-30°, *p*-MeC₆H₄, *p*-MeNC₆H₄, Et, 95.1, 145°,
p-MeC₆H₄, *p*-MeCHC₆H₄, Et, 57.0, 110-11°, *p*-MeOC₆H₄,
p-MeC₆H₄, Et, 88.5, 127-8°, and Ph, *p*-MeNC₆H₄, Me,
28.9, 127°. Addn. of 4 g. $(EtO)_2PS_2H$ to 2.29 g. BzH gave
a slight rise in temp. augmented by addn. of a little EtONa-
EtOH; after 15 min. on a steam bath followed by 1 day at

room temp. there was obtained 1 g. solid, presumably $(EtO)_2$ -
 $P(S)SCH(OH)Ph$, m. 104°. *p*-ClC₆H₄N:CHPh with
 $(EtO)_2PS_2H$ in EtO gave a solid, m. 119-20°, identified as
p-ClC₆H₄NH₂HS₂P(OEt)₂, which apparently formed by hy-
drolysis of the anil in contact with moisture. The salt
was readily prepd. from the 2 components on mixing; simi-
larly were prepd. the following salts: *PhNH_2*HS₂P(OEt)₂,
m. 80°, *p*-MeC₆H₄NH₂HS₂P(OEt)₂, m. 67-8°, and *p*-Cl-
H₂NH₂HS₂P(OEt)₂, m. 116-17°. Since the anils were so
readily attacked by moisture, the following technique was
used for prepn. of the dithiophosphoric esters from the
chloro. derivs.: 2.07 g. *p*-ClC₆H₄NH₂ in dry MePh was
treated with 1.75 g. BzH, the mixt. heated briefly on a steam
bath without access to atm. moisture, and the solvent re-
moved *in vacuo*; the residual anil was treated with 3 g.
 $(EtO)_2PS_2H$, and the mixt. stirred a few min. and allowed
to crystallize in an open dish, yielding 6.3 g. *p*-ClC₆H₄-
NHCH(Ph)SP(S)(OEt)₂, m. 96-7°. Similarly was prepd.
90% *p*-ClC₆H₄NHCH(C₆H₄Me-*p*)SP(S)(OEt)₂, m. 93°. Although a reaction evidently took place between $(EtO)_2$ -
PS₂H and *p*-MeC₆H₄CHO or *p*-MeCHC₆H₄CHO in the
presence or absence of NaOR, no cryst. products could be
isolated.

G. M. Kosolapoff

Pudovik, A.N.

New method of synthesis of esters of phosphonic and
thiophosphonic acids. XXIII. Addition of phosphono-
acetic ester, phosphonoacetone and its homologs to un-
saturated compounds. A. N. Pudovik and N. M.
Lebedeva. *J. Gen. Chem.* ~~U.S.S.R.~~ 25, 1803-6 (1955).
(Engl. translation).—See *C.A.* 50, 8442c. B. M. R.

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Pudovik, A. N.

New method of synthesis of esters of phosphonic and thiophosphonic acids. XXIII. Addition of phosphonoacetic ester, phosphonoacetone, and its homologs to unsaturated compounds. A. N. Pudovik and N. M. Lebedeva (Kavala Branch Acad. Sci. USSR). *Zhur. Obshchei Khim.* 25, 1920-1 (1955); cf. *C. A.* 48, 584h; 56, 7073i. To the Na deriv. prepd. from 1.70 g. Na and 15 g. $\text{AcCH}_2\text{P}(\text{O})(\text{OEt})_2$ was added 13 g. MeI in Et_2O . After refluxing 5 hrs. there was obtained 11.6 g. $\text{AcCHMeP}(\text{O})(\text{OEt})_2$, b_p 109-11°, n_D²⁰ 1.4335, d₄ 1.084. Similarly, 3.91 g. K, 19.6 g. $\text{AcCH}_2\text{P}(\text{O})(\text{OEt})_2$ and 15.6 g. EtI gave 14.8 g. $\text{AcCH}_2\text{P}(\text{O})(\text{OEt})_2$, b_p 128-9°, n_D²⁰ 1.4370, d₄ 1.0724. These alkylation products and $\text{EtO}_2\text{CCH}_2\text{P}(\text{O})(\text{OEt})_2$ were added to esters and nitriles of unsatd. carboxylic acids under the influence of RONa as catalyst; since these addns. were sluggish, a reflux period of 0.5-1 hrs. was necessary to attain the yields indicated below. Thus were obtained (b.p., n_D²⁰, and d₄

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given): 81.5% combined yield of $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$, b_p 167-8°, 1.4410, 1.1368, and $(\text{EtO})_2\text{P}(\text{O})\text{C}(\text{CO}_2\text{Et})(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$, b_p 199-200°, 1.4550, 1.1712; 22% $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CHMeCN}$, b_p 166-7°, 1.4418, 1.1045; 17% $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CHMeCH}_2\text{CO}_2\text{Et}$, m 75-6°, 67.8% $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CHMeCH}_2\text{CN}$, b_p 164°, 1.4458, 1.1144 (from vinylacetonitrile, which isomerized under action of the basic catalyst); 54% combined yield of $(\text{EtO})_2\text{P}(\text{O})\text{CHAcCH}_2\text{CH}_2\text{CO}_2\text{Me}$, b_p 166-2°, 1.4488, 1.1347, and $(\text{EtO})_2\text{P}(\text{O})\text{CAdCH}_2\text{CH}_2\text{CO}_2\text{Me}$, b_p 188-92°, 1.4582, —; 57.5% $(\text{EtO})_2\text{P}(\text{O})\text{CHAcCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CO}_2\text{Et}$, b_p 183-4°, 1.4500, 1.1725; 10% $(\text{EtO})_2\text{P}(\text{O})\text{CHAcC}(\text{CO}_2\text{Et})\text{CHCO}_2\text{Et}$, b_p 183°, 1.4670, —; 70.5% $(\text{EtO})_2\text{P}(\text{O})\text{CEIAcCH}_2\text{CH}_2\text{CN}$, b_p 185°, 1.4577, 1.1022. Hydrolysis of several of the above esters resulted in formation of uncrystallizable sirups only. G. M. Kosolapoff.

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Pydlovik, A.N.

Anomalous reaction of α -halo ketones with triethyl ester of phosphorous acid. A. N. Pydlovik (Chem. Inst., Acad. Sci. U.S.S.R., Kazan). *Dokl. Akad. Nauk SSSR* 25: 2173-82 (1955); cf. C.A. 50, 3219g. To 35 g. $(EtO)_3P$ (Ia) at 120° was added

dropwise 18.5 g. $ClCH_2Ac$; after 1 hr. at 100° the mixt. was distd. yielding 23.8 g. $(EtO)_2P(O)OCH_2CH_3$ (I), b_p 96°, n_D^{20} 1.4190, d_4^{20} 1.0708. I (10 g.) heated with 0.2 g. Na in 15 ml. dry EtOH gave a distillate of 1.55 g. Me_2CO and 8.45 g. Ia. Hydrolysis of I with 30% H_2SO_4 gave Me_2CO and H_3PO_4 . Ia (93 g.) mixed with 76.9 g. $BrCH_2Ac$ at 110-20° and heated 1 hr. at 150-70° gave 15 g. I and 75 g. $AcCH_2P(O)(OEt)_2$ (II), b_p 126°, n_D^{20} 1.4350, d_4^{20} 1.1252 (phenylhydrazone, b_p 193°). Similarly 31 g. Ia and 25.6 g. $BrCH_2Ac$ in 50 ml. Et_2O refluxed 3 hrs. gave 13.8 g. I and 4.8 g. II. Heating 40 g. Ia with 41 g. ICH_2Ac in 100 ml. Et_2O 1 hr. gave 33 g. II, 2.7 g. I, and 2.2 g. $(EtO)_2P(O)OH$. $BrCH_2Bz$ (46.5 g.) and 40 g. Ia in 25 ml. C_6H_6 reacted vigorously, then heated 0.5 hr. on a steam bath and distd. gave 34.7 g. $BzCH_2P(O)(OEt)_2$ (III), b_p 102-2.5°, n_D^{20} 1.5137, d_4^{20} 1.1760, and 0.1 g. $(EtO)_2P(O)OCH_2Ph$ (IV), b_p 171°, n_D^{20} 1.5009, d_4^{20} 1.1422. Similarly 30 g. Ia and 32 g. $BrCH_2Bz$ in Et_2O at reflux gave 21.6 g. III and 13.8 g. IV. Ia and $ClCH_2Bz$ at 130-40° gave only IV, while ICH_2Bz in Et_2O gave III and a little IV. IV and $EtOH-EtONa$ slowly distd. gave $AcPh$, but III gave only a slight reaction with $EtONa$. Hydrolysis of III with 1:1 HCl at 140° gave $BzCH_2PO_3H_2$, m. 113°, which heated 6 hrs. at 220-30° with 1:1 HCl gave $AcPh$ and H_3PO_4 . IV

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with 1:1 HCl rapidly yielded AcPh. 2-Chlorocyclohexanone (V) and Ia yielded on heating to 140° only *di-Et 1-cyclohexenyl phosphate*, b_p 143°, n_D^{20} 1.4523, d_4^{20} 1.1032, which heated with EtOH-EtONa readily gave cyclohexanone and $(EtO)_2PO$. V (23 g.) and $(EtO)_2PONa$, from 3.8 g. Na, in Et₂O gave 25.5 g. *di-Et cyclohexanone-2-phosphonate*, b_p 126°, b_m 146°, n_D^{20} 1.4576, d_4^{20} 1.1352; the free acid was a syrup; the phosphonate is much less rapidly hydrolyzed by HCl.

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Pudovik, A.N.

Chem ✓ Synthesis of esters of phosphonic and thiophosphonic acids. XXIV. Addition of phosphonoacetonitrile and its homologs to esters and nitriles of unsaturated carboxylic acids. A. N. Pudovik and N. M. Lebedeva. *J. Gen. Chem. U.S.S.R.* 25, 2199-2202(1955)(Engl. translation). See *C.A.* 50, 0280d. *B. M. B.* *Z*

PUDOVIK, A.N.

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Synthesis of esters of phosphonic and thionosphonic acids. XXIV. Addition of phosphonoacetonitrile and its homologs to esters and nitriles of unsaturated carboxylic acids. A. N. Pudovik and N. M. Leshchova. Zhur. Obshchei Khim. 29: 2235-40 (1955); cf. C.A. 49: 8788; 50: 8442c. — To $(EtO)_2P$ was added $ClCH_2CN$ at 130-40°; distn. gave 80-5% $(EtO)_2P(O)CH_2CN$ (I), b_p 126-7°, n_D^{20} 1.4310, d_4^{20} 1.1312. This (7-10 g.) and equimolar amt. of unsatd. ester or nitrile treated with satd. $EtONa-EtOH$ (1 drop to several ml.), then heated on a steam bath several hrs. gave the following esters (% yield, b_p , n_D^{20} , and d_4^{20} given): $(EtO)_2P(O)C(CN)CH_2CH_2CN$, 82; — (m. 75-6°). —; $(EtO)_2P(O)CH(CN)CHMeCH_2CN$, 53.2; b_p 170°, 1.4503, 1.1129; $(EtO)_2P(O)CH(CN)CH_2CH_2CO_2Me$, b_p 183-5°, 1.4470, 1.1570, and $(EtO)_2P(O)C(CN)CH_2CH_2CO_2Me$, b_p 183-5°, 1.4470, 1.1570, and $(EtO)_2P(O)C(CN)CH_2CH_2CO_2Me$, 50.3 (combined), b_p 195°, 1.4535, —; $(EtO)_2P(O)CH(CN)CH_2CH_2CO_2Me$, b_p 165-7°, 1.4410, 1.1175, and $(EtO)_2P(O)C(CN)CH_2CH_2CO_2Me$, 46.8 (combined), b_p 177-80°, 1.4490, 1.1242; $(EtO)_2P(O)CH(CN)CH_2CH_2CO_2Bu$, 58, b_p 199°, 1.4450, —; $(EtO)_2P(O)CH(CN)CHMeCH_2CO_2Et$, 40.5, b_p 158-60°, 1.4440, 1.1058; $(EtO)_2P(O)CH(CN)CH(CO_2Et)CH_2CO_2Et$, 71.3, b_p 194°, 1.4380, —; $(EtO)_2P(O)CH(CN)CHPhCH_2CO_2Et$, 26.3, b_p 201-2°, 1.4815, 1.1250. I heated with K in Et_2O -dioxane

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1-2 hrs., followed by alkyl natrium and heating 3-6 hrs. gave the alkylated esters: $(EtO)_2P(O)CHMeCN$, 87.5, b_1 140-1°, 1.4310, 1.0861; $(EtO)_2P(O)CHPhCN$, 53, b_1 119°, 1.4328, 1.076; $(EtO)_2P(O)CHPhCN$, 73.5, b_1 151°, 1.4305, 1.0578; $(EtO)_2P(O)CHCNCHMe$, 40.18, b_1 140-7°, 1.4378, 1.0551; $(EtO)_2P(O)CHBuCN$, 48.4, b_1 160-2°, 1.4378, 1.0401; $(EtO)_2P(O)CH(CN)CH_2CH_2CH_3$, 73.3, b_1 154°, 1.4482, 1.0777; $(EtO)_2P(O)CH(CN)CH_2CH_2CH_2Ph$, 53, b_1 170-1°, 1.5000, —; $(EtO)_2P(O)C(CN)(CH_2Ph)_2$, —, b_1 210-15°, 1.5275, —. Addn. of these to unsatd. compounds with $EtONa$ catalyst gave: $(EtO)_2P(O)CH(CN)CH_2CH_2CO_2Me$, 90.8, b_1 167°, 1.4490, 1.1120; $(EtO)_2P(O)C(CN)(CH_2CHMeCO_2Bu)Pr$, 75.2, b_1 168°, 1.4480, 1.0381; $(EtO)_2P(O)C(CN)CH_2CH_2CN$, 42.6, b_1 175°, 1.4620, 1.0977; $(EtO)_2P(O)C(CN)Bu(CH_2CH_2CN)$, 78.3, b_1 180°, 1.4550, 1.0669.

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PUDOVIK, A. N.

USSR/Chemistry - Organic chemistry

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Authors : Pudovik, A. N., and Lebedeva, N. M.

Title : About the reactions of chloro- and bromoacetone with triethylphosphite

Periodical : Dok. AN SSSR 101/5, 889-892, Apr 11, 1955

Abstract : The synthesis of phosphonium in two tautomeric forms as a product of reaction between chloro- and bromoacetone and triethylphosphite is announced. It was established that the methylene group in phosphonacetone is connected with the phosphonium and acetyl groups which should warrant sufficient mobility of its hydrogen atoms and also increase the ability of the phosphonacetone toward addition reactions. The physico-chemical properties of the triethylphosphite reaction products are listed. Eight references: 5 USSR, 2 USA and 1 German (1930-1954).

Institution : Acad. of Sc., USSR, Kazan Branch, The A. Ye. Arbuzov Chem. Inst.

Presented by : Academician B. A. Arbuzov, November 9, 1954

PUDOVIK, A.N.; IVANOV, B.Ye.

Hypochlorination and oxidation of piperylene. Dokl. AN SSSR 103
no.3:443-444 J1'55. (MLRA 8:11)

1. Kazanskiy gosudarstvennyy universitet imeni V.I.Ul'yanova-Lenina.
Predstavleno akademikom B.A. Arbuzovym
(Piperylene)

Pudovik, A. N.

Anomalous reaction of α -halo ketones with esters of phosphorous acid, A. N. Pudovik (Kazan Branch, Acad. Sci., U.S.S.R.), Dokl. Akad. Nauk S.S.S.R. 185, 735-7 (1955); cf. C.A. 50, 3219c. At low temp. in Et₂O, ICH_2Ac and $(\text{EtO})_2\text{P}$ gave 82.6% of 99/10 mixt. of $\text{AcCH}_2\text{PO}_2\text{Et}$ and $\text{CH}_2\text{CH}_2\text{CMcOPO}(\text{OEt})_2$; BrCH_2Ac similarly gave 20/80 mixt. while ClCH_2Ac at 100-20° (lower temp. does not induce the reaction) gave 93.9% isopropenyl ester. BrCH_2Ac or ClCH_2Ac at 155-60° gave 80% and 11.9% phosphate with a corresponding decline in yield of the unsaid. phosphate ester. Other $(\text{RO})_2\text{P}$ gave similar results. Prepd. were: $\text{AcCH}_2\text{PO}(\text{OMe})_2$, b_p 123-4°, n_D²⁰ 1.4337, d₄²⁰ 1.1748; $\text{CH}_2\text{CH}_2\text{CMcOPO}(\text{OMe})_2$, b_p 84-5°, 1.4175, 1.1449; $\text{AcCH}_2\text{PO}(\text{OBu})_2$, b_p 149-50°, 1.4315, 1.0152; $\text{CH}_2\text{CH}_2\text{CMcOPO}(\text{OBu})_2$, b_p 125-6°, 1.4268, 1.0049; $(\text{iso-BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$, b_p 133-4°, 1.4335, 1.0246; $(\text{iso-BuO})_2\text{POOCMe:CH:}$, b_p 122-3°, 1.4245, 0.9055. Reactions of α , α - and α , γ -dihalo ketones yield mainly "anomalous" products; AcCHCl_2 gave 70-83% diethyl 3-chloro-2-isopropenyl phosphate, b_p 110.5-7°, 1.4370, 1.1833, and diethyl 3-chloro-2-isopropenyl phosphate, b_p 154-5°, 1.4400, 1.0802. The former on chlorination gave 85% di-Et 1,2,3-trichloropropyl phosphate, b_p 147-8°, 1.4550, 1.3414. AcCHBr_2 gave similar results. $\text{CO}(\text{CH}_2\text{Cl})_2$ and $\text{CO}(\text{CH}_2\text{Br})_2$ gave $\text{ClCH}_2\text{C}(\text{CH}_3)\text{OPO}(\text{OEt})_2$ and $\text{CO}(\text{CH}_2\text{Cl})_2$ gave $\text{ClCH}_2\text{C}(\text{CH}_3)\text{OPO}(\text{OEt})_2$, b_p 142.5-3°, 1.4622, 1.3028. Ozonolysis of these gave CH_3O , confirming the structure; chlorination confirmed with $(\text{EtO})_2\text{P}$ gave $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)\text{OPO}(\text{OEt})_2$, b_p 193-5°, 1.4435, 1.1623; transesterification of this with EtOH

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gave Et_2PO and $\text{AcCH}_2\text{PO}(\text{OEt})$. Halo ketones with more electroneg. substituents on the chain yield higher proportions of unsatd. phosphate product in reactions with $(\text{RO})_2\text{P}$. Ac_2CHCl gave 66-80% $\text{MeC}(\text{CH}_2\text{Ac})\text{OPO}(\text{OEt})_2$, b_p 110-20°, 1.4480, 1.1237, and the *di-iso-Bu ester*, b_p 137-8°, 1.4468, 1.0425. Dichloroacetylacetone gave 63% *di-Et chloroisopentenonyl phosphate*, b_p 135°, 1.4626, 1.2292, or 80% *di-iso-Bu ester*, b_p 160-1°, 1.4575, 1.1240; addn. of chlorine to the 1st of these gave 100% *di-Et trichloroisopentenonyl phosphate*, b_p 151°, 1.4672, 1.3431. $(\text{RO})_2\text{P}$ reacts readily with $\text{AcCHClCH}_2\text{Et}$ or $\text{AcCClCO}_2\text{Et}$; thus obtained were: $\text{EtCO}_2\text{CH}:\text{CMcOP}(\text{OEt})_2$, b_p 155-8°, 1.4451, 1.1349; *di-iso-Bu ester*, b_p 175°, 1.4445, 1.0569; $\text{EtO}_2\text{CC}(\text{CH}_2)\text{CMcOP}(\text{OEt})_2$, b_p 136°, 1.4572, 1.1203; *di-iso-Bu ester*, b_p 154°, 1.4547, 1.1289. Treatment of $\text{AcCH}_2\text{PO}(\text{OEt})_2$ with SO_2Cl_2 gave 61% α -chloro(diethylphosphono)acetone, b_p 131-2°, 1.4484, 1.2233, which with $(\text{EtO})_2\text{P}$ gave *di-Et diethylphosphonoisopropenyl phosphate*, b_p 161-2°, 1.4478, 1.1762. The structures of the products were confirmed by chlorination, bromination and transesterification (cf. Perkow, et al., C.A. 50, 3213h).

G. M. Kosolapoff

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Podovik, A. N.

Phosphonoethylation of mercaptans, dialkyl phosphonates and alkylphosphonic acids. A. N. Podovik and M. M. Zakharova (State Univ., Kazan). Doklady Akad. Nauk SSSR, 1955, No. 3, 3-12 (1955). — To 7 g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{P(O)(OEt)}_2$ and 4.8 g. PhSH was gradually added satd. EtONa in EtOH maintaining the temp. below 50–5°; distn. of the mixt. gave 7.8 g. $\text{PhSCH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 203–4°, n_D^{20} 1.5270, d_4^{20} 1.1440 (n_D^{20} and d_4^{20} listed for the compds. below).
Similarly, 1-methoxy-3-pentene-5-thiol gave 70% $\text{MeOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 185–7°, 1.4829, 1.0723, while 1-ethoxy-3-pentene-5-thiol gave 62% $\text{EtOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 191–2°, 1.4798, 1.0499, and 2-butene-4-thiol gave 65% $\text{MeCH}_2\text{CHCH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 120–2°, 1.4680, 1.0136. Similar reaction of 6.8 g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{P(O)(OEt)}_2$ and 5.5 g. (EtO)₂PSH in the presence of EtONa-EtOH gave 7.8 g. $(\text{EtO})_2\text{P(S)CH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 163°, 1.4638, 1.1356; (BuO)₂PSH gave 67% $(\text{BuO})_2\text{P(S)CH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 209°, 1.4510, 1.0573, while EtP(O)(OEt)_2 gave 59% $\text{EtP(O)(OEt)}_2\text{CH}_2\text{CH}_2\text{P(O)(OEt)}_2$, b_p 195°, 1.4510, 1.1235.
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PUDOVIK, A.N.

PUDOVIK, A.N.; ZAKHAROVA, M.M.

Phosphonoethylation of mercaptans of dialkylphosphorous acid and
alkylphosphinous acid. Uch.zap.Kaz.un. 115 no.3:3-12 '55.
(MLRA 10:5)

1.Kafedra sinteticheskogo kauchuka.
(Mercaptans) (Phosphorous acid) (Phosphinous acid)

PUDOVIK, A.N. (Kazan')

Addition of incomplete esters of phosphorus acids to unsaturated
compounds. Uch.zap.Kaz.un. 115 no.10:40-43 '55. (MLRA 10:5)
(Phosphorus acids)
(Unsaturated compounds)

PUDOVIK, A.N.; ARBUZOVA, M.P.

Synthesis and isomerization of phenyl ethers of ethoxy- and
butoxypentenols. Uch.zap.Kaz.un. 116 no.1:136-140 '55.
(MLRA 10:5)

1. Kafedra sinteticheskogo kauchuka.
(Chemistry, Organic--Synthesis)
(Isomerization) (Ether)

PUDOVIK, A.M.; IVANOV, B.Ye.

Addition of ethyl alcohol to isoprene oxide. Uch.zap.Kaz.un. 116
no.1:141-144 '55. (MLRA 10:5)

1.Kafedra sinteticheskogo kauchuka.
(Isoprene) (Rubber, Synthetic) (Ethyl alcohol)

PUDOVIK, A. N.
USSR/General Questions

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Abs Jour: Ref Zhur-Khimiya No. 7, 1957, 21877

Author : Neslerova, N. M. and Pudovik A. N.

Inst : None

Title : Boris Aleksandrovich Arbuzov, (Bibliography)

Orig Pub: M. AN SSSR 1956, 48 p., 1 rouble

Abstract: No Abstract

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SECRET

"Anomalous Reaction of Haloketones with Esters of Thionous Acid"
presented at the First Conference on Thionous Compounds,
Tashkent, 2-10 Dec 1961

1: 2-3, 11/41

PUDOVIK, A. N.

✓ Anomalous reaction of α -halo ketones with esters of phosphorous acid: II. Reaction of chloro- and bromoacetone with esters of phosphorous and phenylphosphonous acids. A. N. Pudovik and V. P. Aver'yanova (State Univ., Kazan). *Zhur. Obshchei Khim.* 26, 1426-31 (1950); cf. C.A. 50, 8486i. — Dropwise addn. of 22.1 g. AcCH_2Br to 20 g. $(\text{MeO})_2\text{P}$ preheated to 110–15°, followed by 0.5 hr. at 120° gave 10.5 g. $(\text{MeO})_2\text{P}(\text{O})\text{OCMe} \cdot \text{CH}_2$ (I), b_p 84–5°, d₂₀ 1.1449, n_D²⁰ 1.4175, and 8.4 g. $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$ (II), b_p 123–4°, d₂₀ 1.1748, n_D²⁰ 1.4337. Careful heating of 24 g. $(\text{MeO})_2\text{P}$ and 25.2 g. AcCH_2Cl to 70° started a vigorous reaction kept at 80° by cooling; distn. gave 30 g. I and 1.7 g. II; a similar reaction at 110° gave, from 30 g. $(\text{MeO})_2\text{P}$, 25.4 g. I and 0.6 g. II. Distn. of 0.2 g. Na in 15 ml. dry MeOH and 10 g. I gave MeOH and Me_2CO , as well as 2.5 g. $(\text{MeO})_2\text{PO}$. Heating 40 g. $(\text{EtO})_2\text{P}$ and 22 g. AcCH_2Cl to 95° started a vigorous reaction completed by 0.5 hr. at 110–20°, yielding 26 g. di-Et analog of I and 1.7 g. di-Et analog of II, b_p 127–9°, n_D²⁰ 1.4350; slow addn. of 13.8 g. AcCH_2Cl to 25 g. refluxing $(\text{EtO})_2\text{P}$ gave 2.7 g. di-Et analog of II and 20 g. di-Et analog of I. Ozonization of the di-Et analog of I in CCl_4 and treatment with hot H_2O gave CH_3O . Heating 30 g. $(\text{BuO})_2\text{P}$ and 11 g. AcCH_2Cl to 135–45° gave 15.8 g. $(\text{BuO})_2\text{P}(\text{O})\text{OCMe} \cdot \text{CH}_2$, b_p 125–8°, d₂₀ 1.0049, n_D²⁰ 1.4268, and 2.5 g. $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$, b_p 149–50°, n_D²⁰ 1.4322. Addn. of 10.4 g. AcCH_2Br to 30 g. $(\text{BuO})_2\text{P}$ at 145–55° gave 7.6 g. $(\text{BuO})_2\text{P}(\text{O})\text{OCMe} \cdot \text{CH}_2$, and 13.9 g. $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$, b_p 137–8°, d₂₀ 1.0152, n_D²⁰ 1.4315. Heating 40 g. $(\text{iso-BuO})_2\text{P}$ with 15 g. AcCH_2Cl to 115–20°, finally 125°, gave 30 g. $(\text{iso-BuO})_2\text{P}(\text{O})\text{OCMe} \cdot \text{CH}_2$, b_p 122–3°, d₂₀ 0.9955, n_D²⁰ 1.4245, and 2 g. $(\text{iso-BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$, b_p 145–7°, n_D²⁰ 1.4330; the same reaction at 160° gave 25.7 g. phosphate ester and 6 g. phosphonate; slow addn. of 10.9 g. AcCH_2Br to 20 g. $(\text{iso-BuO})_2\text{P}$ at 155° gave 2.5 g. phosphate ester and 9.5 g. phosphonate, b_p 133–4°, d₂₀ 1.0246, n_D²⁰ 1.4335; the former distd. with iso-BuONa - iso-BuOH gave

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Me₂CO and (iso-BuO)₂PO, b₁₂ 134-5°, n_D²⁰ 1.4195, d₄ 0.985. Hydrolysis of diisobutylpropenyl phosphate with 30% H₂SO₄ readily gave Me₂CO. To 28 g. PhP(OMe)₂, preheated to 90° was slowly added 15.2 g. AcCH₂Cl (vigorous action) and after completion of reaction under 120° there was obtained 18.5 g. PhP(O)(OMe)OCH₂CH₃ (III), b₁₂ 137-8°, d₄ 1.1421, n_D²⁰ 1.5120, and 2.5 g. material b₁₂ 165-70°, n_D²⁰ 1.5216; under these conditions AcCH₂Br gave only tar. Reaction of 20 g. PhP(OMe)₂ and 18 g. AcCH₂Br in Et₂O gave 3.8 g. III, b₁₂ 137-9°, n_D²⁰ 1.5135, and 5 g. PhP(O)(CH₂Ac)OMe, b₁₂ 189-70°, d₄ 1.1965, n_D²⁰ 1.5220, with much tar. To (EtO)₂PONa from 100 g. (EtO)₂POH, 14.4 g. Na, and 200 ml. Et₂O was slowly added 57.6 g. AcCH₂Cl; after 3 hrs. refluxing and centrifugal sepn. of NaCl there was obtained 50 g. product, b₁₂ 50-94°, 6 g. product, b₁₂ 94-8°, and 7 g. product, b₁₂ 122-9°, n_D²⁰ 1.4345; it was impossible to isolate individual products. Similar reaction with 50 g. (EtO)₂POH, 7 g. Na; and 42.8 g. AcCH₂Br in ligroine gave 9 g. (EtO)₂P(O)CH₂Ac, b₁₂ 131°, n_D²⁰ 1.4320, and lower boiling fractions; the results were the same in Et₂O, C₆H₆, or MePh.

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Pudovik, A. N.

III. Reaction of α, α - and α, γ -dibromo ketones with triethyl phosphite. A. N. Pudovik and L. G. Sulekhova (State Univ., Kazan). *Zh. Obshch. Khim.* 26, 1431-4 (1953).—Addn. of 40 g. $(EtO)_3P$ to 31.3 g. $CO(CH_2Cl)_2$, preheated to 120° gave 25.2 g. $(EtO)_3P(O)OC(CH_2Cl)_2$; CH_2 (I), b_p 133.5–1.5°, d₄ 1.1034, n_D²⁰ 1.4435, and 4.5 g. higher-boiling fraction which was not purified. Chlorination of above unsatd. ester in CCl_4 with ice cooling gave a good yield of $(EtO)_3P(O)OCCl(CH_2Cl)_2$; b_p 150–2°, d₄ 1.3593, n_D²⁰ 1.4631. Addn. of 63 g. $(EtO)_3P$ to 80.0 g. $CO(CH_2Br)_2$, preheated to 120° gave 40 g. $EtBr$ and 42.2 g. $(EtO)_3P(O)OC(CH_2Br)_2$; CH_2 (II), b_p 142.5–3°, d₄ 1.3028, n_D²⁰ 1.4622; the residue was undistillable. A similar reaction at $20-6^\circ$ gave only the unsatd. ester above. Chlorination of the unsatd. ester as above gave a good yield of $(EtO)_3P(O)OCCl(CH_2Br)_2$; b_p 159°, d₄ 1.5103, n_D²⁰ 1.4733. Ozonolysis of II gave CH_2O . Heating 7.45 g. I with 7 g. $(EtO)_3P$ 4 hrs. at 240° in sealed tube gave 5.4 g. $(EtO)_3P(O)OC(CH_2)_2CH_2P(O)(OEt)_2$; b_p 193–5°, d₄ 1.1623, n_D²⁰ 1.4435, which formed readily from II and $(EtO)_3P$ refluxed 5 hrs.; the product in this case, b_p 195–7°, d₄ 1.1645, n_D²⁰ 1.4440. Mixing 25.2 g. $AcCHCl_2$ and 33.2 g. $(EtO)_3P$ gave a spontaneous reaction (temp. rise to 120°); final heating to 110° completed the reaction yielding 37.3 g. $(EtO)_3P(O)OCMe_2CHCl_2$; b_p 116.5–17°, d₄ 1.1833, n_D²⁰ 1.4370, which chlorinated in CCl_4 with ice cooling to a good yield of $(EtO)_3P(O)OCClMeCHCl_2$; b_p 147–8°, d₄ 1.3414, n_D²⁰ 1.4580. A similar reaction of 15 g. $(BuO)_3P$ with 8 g. $AcCHCl_2$ gave 13.6 g.

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(BuO)₃P(O)OCMe: CHCl₃, b_m 164-5°, d₂₀ 1.0892, n_D²⁰ 1.4400.
Heating 0.2 g. Na in 15 ml. dry EtOH with 5.4 g. (EtO)₃P-
(O)OC(C₂H₅)CH₂P(O)(OEt)₂ gave 0.7 g. (EtO)₃PO and 0.8
g. (EtO)₃P(O)CH₂Ac, b_m 130-7°, n_D²⁰ 1.4352. Addn. of 30
g. CO(CH₂Br)₂ to an Et₂O soln. of 6.3 g. Na in 38.3 g.
(EtO)₃POH gave after sepn. of NaBr 9.5 g. unidentified
halogen-free product, b_m 87-9°, d₂₀ 1.0624, n_D²⁰ 1.4060, and a
1.1-g. fraction, b_m 117-27°, d₂₀ 1.0914, n_D²⁰ 1.4310. To 26
g. AcCHBr₂ at 120° was added 20 g. (EtO)₃P with cooling;
there was formed 11.6 g. (EtO)₃P(O)OCMe: CHBr₂, b_m 120-
7°, d₂₀ 1.3043, n_D²⁰ 1.4610, which chlorinated as above gave a
good yield of (EtO)₃P(O)OCMeClCHBrCl, b_m 161-5°, d₂₀
1.4097, n_D²⁰ 1.4735.

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PUDOVIK, A. N.

Anomalous reaction of α -halo ketones with esters of phosphorous acid. II. Reaction of chloro- and bromoacetone with esters of phosphorous and phenylphosphonous acids. A. N. Pudovik and V. P. Aver'yanova. J. Gen. Chem. U.S.S.R. 26, 1805-9 (1950) (English translation). — See C.A. 50: 14512f. III. Reaction of α,α - and α,γ -dihalo ketones with triethyl phosphite. A. N. Pudovik and L. G. Salekhova. Ibid. 1811-14. — See C.A. 50, 14513c. B.M.R.

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PUDOVIK, A. N. ; ALTUNINA, N.

Addition of α -haloethers to isoprene. Zhur.ob.khim. 26 no.6:
1635-1639 Je '56. (MIRA 11:1)

1. Kazanskiy gosudarstvennyy universitet,
(Isoprene) (Ethers)

PUDOVIK, A.N.

Chem ✓ New method of synthesis of esters of phosphonic and thiophosphonic acids. XXV. Addition of mixed dialkyl phosphites, dialkyl thiophosphites and dialkyl phosphite to unsaturated compounds. A. N. Pudovik and N. I. Khlyupina (State Univ., Kazan). Zhur. Obshch. Khim. 26, 1072-7 (1950); cf. C.A. 50, 9380d. Heating 1 mole $(EtO)_2PSH$ with 1.5-2.5 moles ROH with a few drops of H_2PO_4 2 hrs. at 160-65° gave the following esters: 32% $EtO(BuO)PSH$, b. 72-3°, n_D^{20} 1.4040, d_4^{20} 1.0325; 31.5% $EtO(iso-BuO)PSH$, b. 70-2°, 1.4605, 1.0287; 38.7% $EtO(iso-AmO)PSH$, b. 81.5-2.5°, 1.4480, 1.0032. An equimolar mixt. of one of the above esters and the desired unsatd. compd. was slowly treated with satd. $EtONa-EtOH$ until the exothermic reaction ceased, heated 0.5 hr. on a steam bath, and the products were distd. Thus esters of methacrylic, cinnamic and maleic acids, $CH_2=CHMeCN$, mesityl oxide, and various anils yielded the following products: (Y, % yield, b.p./mm. or m.p., n_D^{20} and d_4^{20} given): $EtO(BuO)P(O)Y$: $CH_2=CHMeCO_2Bu$, 69.3, 155-8°/10, 1.4335, 1.0124; $CH_2=CHMeCO_2Et$, 54.1, 177-8°/8, 1.4807, 1.0974; $CH(CO_2Me)CH_2CO_2Me$, 55, 178-8.5° (sic), 1.4405, 1.1435; $CH_2=CHMeCN$, 59.7, 170°/10, 1.4450, 1.0577; $CH_2=CHMe$, 80.6, 135-6°/10, 1.4390, 1.0145; $CH(C_6H_4NO_2-m)NHCH_2Me$, 49.1, m. 122°.

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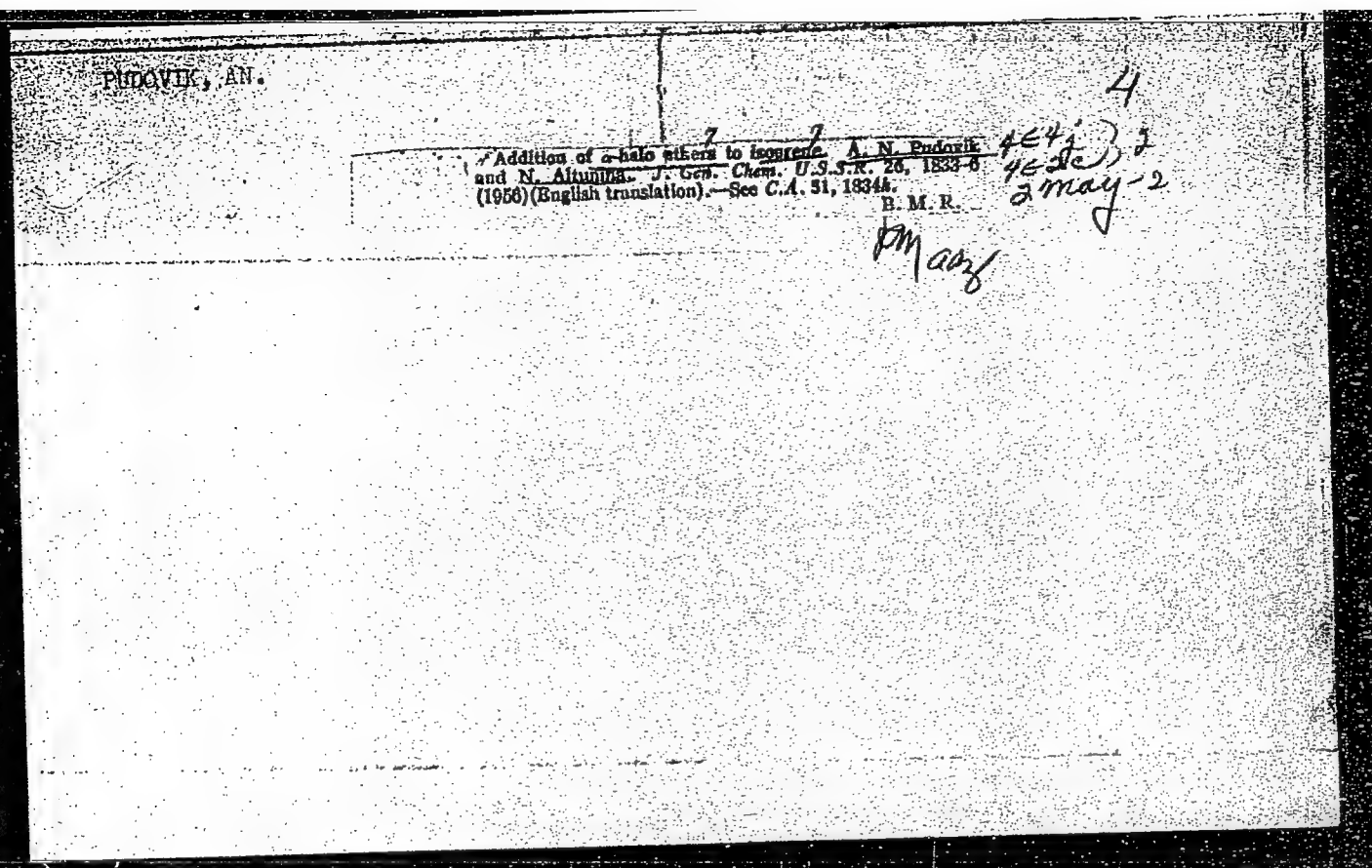
PUDOVIK, A. N.

Pudovik A. N., Khlyupina N. I.

$\text{CH}(\text{NHPh})\text{CH}_2\text{NMe}$, p. 45.8, m. 88°. $\text{CH}_2\text{CHMeCO}_2\text{Bu}$, 70.8, 148°/10, 1.4635, 1.0382; CH_2CHMeCN , 57.3, 176°/10, 1.4350, 0.9787. $\text{EtO}(\text{iso-AmO})\text{P}(\text{O})\text{CMe}_2\text{CH}_2\text{Ac}$, 79.2%, b. 153-4°/10, n_D^{20} 1.4010, d_4^{20} 0.9977. Similarly $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{POH}$ gave the following: $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{P}(\text{O})\text{V}$, % yield, b.p./mm. or m.p., n_D^{20} , d_4^{20} given: $\text{CH}_2\text{CHMeCO}_2\text{Me}$, 67.3, 143-4°/8, 1.4305, 1.0753; $\text{CH}_2\text{CHMeCO}_2\text{Bu}$, 65, 170-7°/8, 1.4582, 1.0573; $\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{CO}_2\text{Me}$, 67.3, 185°/8, 1.4300, 1.1120; $\text{CHPhCH}_2\text{CO}_2\text{Et}$, 62.3, 201-1.5°/8, 1.4960, 1.1190; $\text{CH}(\text{C}_6\text{H}_5\text{NO}_2\text{-m})\text{NHCH}_2\text{Me}$, 53.7, —; $\text{CHNH}(\text{NHPh})\text{C}_6\text{H}_5\text{NMe}_2$, p. 59.5, — (no phys. consts. for the last 2 compds. given). Treatment of crotyl alc. or $\text{CH}_2=\text{CHCH}(\text{OH})\text{Me}$ with PCl_5 failed to yield any $(\text{RO})_2\text{POH}$, as only RCl and H_3PO_4 were obtained. In the prepn. of $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{POH}$ the use of dry allyl alc. and termination of the distn. of the product after some 2% of the material had been distd. are said to be effective means for the prevention of explosions in distn. of the ester. G. M. Kosolapoff.

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PUDOVIK, A.N.

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New method of synthesis of esters of phosphonic and
thiophosphoric acids. XXV. Addition of mixed dialkyl
phosphites, dialkyl thiophosphites, and dialkyl phosphite to
unsaturated compounds. A. N. Pudovik and N. I. Kaban
pina. J. Gen. Chem. U.S.S.R. 20, 1877-80 (1965) (English
translation).—See C.A.B. 51, 3439f. B. M. R.

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Pudovik, A. N.

Hypochlorination of piperylene. A. N. Pudovik and B. E. Ivanov (State Univ., Kazan). *Zhur. Obshchei Khim.* 26, 1910-14 (1956); cf. *C.A.* 50, 5522f. — HOCl adds to

piperylene in 1,2-, 3,4-, and 1,4-positions. Through a suspension of 400 g. chlorinated lime in 5 l. H₂O was passed at 0° for 0.5 hr. a strong stream of CO₂ and 400 g. piperylene was added over 3 hrs.; the mixt. was filtered, satd. with NaCl and extd. with Et₂O yielding 230 g. products, which on fractionation gave 25 g. 3-chloro-4-penten-3-ol (I), b_p 50-1°, n_D²⁰ 1.4570, d₄ 1.0584, 7 g. 5-chloro-2-penten-4-ol (II), b_p 66-7°, n_D²⁰ 1.4685, d₄ 1.0720, and 21 g. 5-chloro-3-penten-2-ol (III), b_p 82-2.5°, n_D²⁰ 1.4760, d₄ 1.0835. Their structures were confirmed by oxidation and ozonolysis. I and Br in CHCl₃ gave 1,2-dibromo-3-chloro-4-pentanol, b_p 136-8°, n_D²⁰ 1.5470; III and Br gave 1-chloro-2,3-dibromo-4-pentanol, b_p 140-9°, m. 69-70°. I heated with Ac₂O in C₆H₆ gave the corresponding acetate, b_p 66-7°, n_D²⁰ 1.4365, d₄ 1.0604; III gave the acetate, b_p 80-9.5°, n_D²⁰ 1.4555, d₄ 1.0790. I and 60% KOH at 160° gave 50% 2,3-epoxy-4-pentene, b. 82-3°, n_D²⁰ 1.4135, d₄ 0.8464. II gave 1,2-epoxy-3-pentene, b. 103-4°, n_D²⁰ 1.4345, d₄ 0.8750, while III gave only tarry products. At 50° in 0.1M aq. soln. in 8 hrs. 41% I hydrolyzes, 47% III, and 7% II.

G. M. K.

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PUDOVIK, A.N.

Anomalous reaction of α -haloketones with phosphorous esters. Part 4:
Reaction of phosphorous esters with mono- and dichloroacetylacetone,
phosphonoacetone and acetoacetic ester. Zhur. ob. khim. 26 no.8:2238-
2243 Ag '56. (MLRA 10:11)

1. Kazanskiy gosudarstvennyy universitet.
(Ketones) (Phosphorous acids)

Pudovik, A. N.

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✓ Anomalous reaction of α -halo ketones with esters of phosphorous acid. IV. Reactions of esters of phosphorous acid with mono- and dichloroacetylacetone, phosphonoacetone, and acetoacetic ester. A. N. Pudovik. *J. Gen. Chem. U.S.S.R.* 26, 2503-8 (1966) (English translation). See *C.A.* 61, 1827b.

B. M. R.

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PUDOVIK, A.N.; IVANOV, B.Ye.

Addition reactions with α -oxides of pentadiene. Zhur. ob. khim.
26 no.10:2768-2771 0 '56. (MIRA 11:3)

1. Kazanskiy Gosudarstvennyy universitet.
(Pentadienes) (Hydrolysis)

Pudovik, A. N.

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Oxidation of butadiene, isoprene and piperylene with acetyl hydroperoxide. A. N. Pudovik and B. E. Ivanov (State Univ., Kazan). *Zhur. Obshch. Khim.* 26, 2771-3 (1950). The rate of oxidation of dienes with AcO_2H rises in the series: butadiene, isoprene, *cis*- and *trans*-piperylene, 2,3-dimethylbutadiene, 2,4-hexadiene. The accumulation of Me groups at the terminal C atoms of butadiene accelerates the reaction more than does a similar accumulation in the middle of the mol. The reaction rate curves are shown. Treatment of 60 g. butadiene in 2 l. Et_2O with 80 ml. 90% AcO_2H at room temp. in 15 days gave 35 g. 1,2-epoxy-3-butene; b. 68-6.5°, d₄ 0.8720, n_D²⁰ 1.4105. Similarly, isoprene with 95% AcO_2H in 12 days gave 1,2-epoxy-2-methyl-1-butene, b. 70.5-80.5°, d₄ 0.8574, n_D²⁰ 1.4180. Mixed *cis*-*trans*-piperylenes (170 g.) in 6 l. Et_2O with 200 ml. 80% AcO_2H in 9 days gave mixed products: 45 g. mixed *cis*-*trans*-3,4-epoxypentene, b. 82-6°, d₄ 0.8472, n_D²⁰ 1.4140, and 34 g. mixed *cis*-*trans*-1,2-epoxy-3-pentene, b. 102-6°, d₄ 0.8752, n_D²⁰ 1.4355. Pure *cis*-piperylene gave the *cis*-3,4-epoxypentene, b. 84.5-6°, d₄ 0.8592, n_D²⁰ 1.4182, and *cis*-1,2-epoxy-3-pentene, b. 103-4°, d₄ 0.8953, n_D²⁰ 1.4385, while *trans*-piperylene gave *trans*-3,4-epoxypentene, b. 82-3.5°, d₄ 0.8432, n_D²⁰ 1.4110, and *trans*-1,2-epoxy-3-pentene, b. 101-2°, d₄ 0.8720, n_D²⁰ 1.4325. Piperylene (68 g.) in 4 l. Et_2O and 100 ml. 85% AcO_2H in 17 days gave 12 g. 3,4-epoxy-1-pentene, 7 g. 1,2-epoxy-3-pentene, and 7 g. piperylene dioxide, b. 66-7°, d₄ 1.0278, n_D²⁰ 1.4295. G. M. K.

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PUDOVIK, A. N.

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New method of synthesis of esters of phosphonic and thiophosphonic acids. XXVI. Addition of partial esters of acids of phosphorus to ethyl isocyanate, diethyl acetate, and esters of unsaturated carboxylic acids. A. N. Pudovik, I. V. Koudonova, and R. B. Kravchenko (State Univ., Kazan). Zhur. Obshchei Khim. 26, 3110-16 (1950); cf. C.A. 49, 9476i; 50, 4808b; 51, 3439. Mixing of (RO)₂POH, RPH(O)OR, or (RO)₂PSH with EtNCO resulted in a slight elevation of temp. but the reaction is evidently very slow. Addn. of dry R₂ONa produced an exothermic reaction, yielding the following esters: 68% EtNHCO₂(OEt), b_p 107-8°, n_D²⁰ 1.4465, d₄²⁰ 1.1294; 65% EtNHCO₂(OEt), b_p 177°, n_D²⁰ 1.4581, d₄²⁰ 1.0589; 39% EtNHCO₂(S)(OEt), b_p 155-6°, n_D²⁰ 1.4811, d₄²⁰ 1.1393. Addn. of (RO)₂POH to esters of HCNS and phenyl and allyl mustard oils in the presence of EtONa resulted in an apparent reaction in each case but the products decomposed during attempted distn. Addn. of R₂ONa to equimolar mixts. of AcOCH₂CH₂ and either (RO)₂PSH or RPH(O)OR gave similarly: 48% EtOPE(O)CH₂CH₂OAc, b_p 110-11°, n_D²⁰ 1.4301, d₄²⁰ 1.0704; 51.5% EtOPE(O)CH₂CH₂OAc, b_p 123°, n_D²⁰ 1.4412, d₄²⁰ 1.0408; 35% EtOP₂(O)CH₂CH₂OAc, b_p 149-50°, n_D²⁰ 1.4990, d₄²⁰ 1.1329; 33% (EtO)₂P(S)CH₂CH₂OAc, b_p 125-7°, n_D²⁰ 1.4580, d₄²⁰ 1.1107 (the mixt. in this case must be heated preliminarily with Et₃N for a satisfactory reaction (cf. above refs.)). Reaction of AcOCH₂CH₂ with (EtO)₂P(O)CH₂CO₂Et, (EtO)₂P(O)CH₂Ac, and (EtO)₂P(O)CH₂CN was performed similarly in the presence of EtONa, requiring 2 hrs. on a steam bath for completion; however, attempted distn. gave either starting materials or decomn. products and tar. Addn. of partial esters of appropriate acids of P to unsatd. carboxylic esters

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A.N. PUDOVIK, I.V. KONVALOVA, R.E. KRIVONOSOVA

gave the following: 84.5% $(EtO)_2P(O)CH_2(CO_2Et)CH_2CO_2Et$, b_p 182°, n_D^{20} 1.4385, d_4^{20} 1.1105; 40% $(EtO)_2P(S)CH_2(CO_2Et)CH_2CO_2Et$, b_p 180-1°, n_D^{20} 1.4508, d_4^{20} 1.1206; 20.1% $(iso-BuO)_2P(S)CH_2(CO_2Et)CH_2CO_2Et$, b_p 186-7°, n_D^{20} 1.4620, d_4^{20} 1.0840; 43.8% $(EtO)_2P(O)CHMeCHMeCO_2Et$, b_p 142-3°, n_D^{20} 1.4330, d_4^{20} 1.0616; 21% $(MeO)_2P(O)CHMeCHMeCO_2Et$, b_p 121-2°, n_D^{20} 1.4260, d_4^{20} 1.0821; 18.8% $(EtO)_2P(O)CHMeCHMeCO_2Et$, b_p 131-2°, n_D^{20} 1.4310, d_4^{20} 1.0622. Addn. of $(RO)_2POH$ to $PhMeC:CHCO_2Et$,

and of $(EtO)_2P(O)CH_2CO_2Et$ to di-Bt citraconate failed.
G. M. Kosolapoff

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USSR/Organic Chemistry - Synthetic Organic Chemistry

E-2

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4297

Author : Pudovik, A.N., Arbuzova, M.P.

Inst : Kazan University

Title : Synthesis and Isomerization of Phenol Ethers of
Ethoxy- and Butoxy-pentenols

Orig Pub : Uch. zap. Kazanskogo un-ta, 1956, 116, No 1, 136-140

Abstract : Study of interaction of $RCCH_2CH_2CH=CHCH_2Cl$ (I) $R = C_2H_5$
or C_4H_9 , and $C_2H_5OCH_2CH_2CHClCH=CH_2$ (II) with C_6H_5OH
(III) and KCH . In aqueous media I and II form
 $ROCH_2CH_2CH=CHCH_2OC_6H_5$ (IV). In acetone solution II yields,
in addition to IV ($R = C_2H_5$), also $C_2H_5-OCH_2CH(OC_6H_5)CH=$
 CH_2 (V).

Card 1/3

- 43 -

FUDOVİK, A. N. (Chem. Inst. im. Acad. A. Ye. Arbuzov, Kazan Affil. AS USSR)

"The Anomalous Reaction of alpha-halogen ketones with Complete Esters of Phosphorous Acid" (Ob anomal'noy reaktsii alpha-galoidketonov s polnymi efirami fosforistoy kisloty)

Chemistry and Uses of Organophosphorous Compounds
(Khimiya i primeneniye fosfororganicheskikh soedneniy),
Trudy of First Conference, 8-10 December 1955, Kazan,
pp. Published by Kazan Affil. AS USSR, 1957
248-261

Report discussed by M. I. Kabachnik (Inst. Element. Organ. Compounds AS USSR),
B. A. Arbuzov (Chem. Inst. im. Acad. A. Ye. Arbuzov, Kazan Affil. AS USSR), and
by author.

Pudovik, A.N.

USSR/General Topics - Methodology, History, Scientific
Institutions and Conferences, Instruction, Problems
Concerning Bibliography and Scientific Documentation.

A-1

Abs Jour : Referat Zhur - Khimiya, No 1, 1958, 12.

Author : A.N. Pudovik

Inst : -

Title : A Glorious Anniversary.

Orig Pub : Zh. obshch. khimii, 1957, No 9, 2313-2328

Abstract : To the 80th anniversary of the birthday and the 50th
anniversary of the scientific activity of academician
A.Ye. Arbuzov.
Biographical sketch and scientific works.
Bibliography with 64 titles.

Card 1/1

Pudovik, A. N.

V New method of synthesis of esters of phosphonic and thiophosphonic acids. XXVII. Addition of dialkyl phosphites and dialkyl thiophosphites to the ylide derivatives of malonic ester and acetylacetic. Phosphono-herbimuric acids. A. N. Pudovik and T. M. Moshkina (State Univ., Kazan). *Dokl. Akad. Nauk* 27, 1611-17 (1967); *Ch.* 47, 9910a; 48, 2572a; 50, 4143; 11230; 51, 8542a; Goldstein and Fiebig, *C.A.* 51, 5769c. To an equimolar mixt. of $\text{CH}_2\text{C}(\text{CO}_2\text{Et})_2$ (cf. Levina and Golovnikov, *C.A.* 50, 2458c) and $(\text{RO})_2\text{POH}$ or $(\text{RO})_2\text{PSH}$ was added a satd. soln. of RONa in ROH ; after the exothermic reaction the mixt. was warmed 15-20 min. on an H_2O bath and distd. yielding: 88% $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$, b_p 173-3°, n_D^{20} 1.4424, d_4^{20} 1.2034; 71% *di-Et ester analog*, b_p 179-80°, 1.4355, 1.1278; 47% $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$, b_p 14410, 1.0750; 51% $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$, b_p 180-2°, 1.4570, 1.1128. Slow addn. of EtONa to EtOH to 10 g. $\text{PhCH}_2\text{C}(\text{Ac})_2$ and 11 g. $(\text{EtO})_2\text{POH}$ gave after a long induction period a rapid exothermic reaction which yielded 4.2 g. $\text{PhCH}(\text{CH}_2\text{Ac})\text{P}(\text{O})(\text{OEt})_2$ (II), b_p 190-1°, 1.5005, 1.1294, formed by evident decarboxylation of the expected product. Similar reactions that involve slow induction periods were observed.

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Distr: 4E4J/4E38/4E20(j)

A. N. Pudovik + t. M. Moshkina etc.

EtONa in 20-30 ml. abs. EtOH with 0.07 mole $\text{CO}(\text{NH}_2)_2$ or $\text{CS}(\text{NH}_2)_2$ and refluxed 6-7 hrs. gave after soln. in H_2O and acidification the corresponding phosphodibarbituric acids. Thus were prepd. in 60-70% yields: $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CONH})_2\text{CO}$, m. 97°; di-Et ester, m. 100°; di-Bu ester, m. 109°; $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CONH})_2\text{CO}$, m. 98-100°; $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CONH})_2\text{CS}$, m. 101°; di-Et ester, m. 162-3°; di-Bu ester, m. 168°; $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CONH})_2\text{CS}$, m. 163-4°; $(\text{MeO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$, m. 105°; $(\text{EtO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$, m. 107°; $(\text{BuO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$, m. 110°; $(\text{EtO})_2\text{P}(\text{S})\text{CHMeCH}(\text{CONH})_2\text{CO}$, m. 144°; $(\text{MeO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CS}$, m. 177°; $(\text{EtO})_2\text{P}(\text{O})\text{CHPhCH}(\text{CONH})_2\text{CO}$, m. 109°; $(\text{EtO})_2\text{P}(\text{S})\text{CHPhCH}(\text{CONH})_2\text{CO}$, m. 110°; $(\text{EtO})_2\text{P}(\text{O})\text{CHPhCH}(\text{CONH})_2\text{CS}$, m. 178°; $(\text{EtO})_2\text{P}(\text{S})\text{CHPhCH}(\text{CONH})_2\text{CS}$, m. 179°. Prepn. of $(\text{RO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{R})_2$ was accomplished by 3 different routes, all of which giving the same product; hence the Arbuzov reaction (cf. A. and Kamal, C.A. 42, 4523g) is normal with halomalonate esters and the supposition about its abnormality made by Allen and Johnson (C.A. 50, 3272k) is incorrect. Heating 16.6 g. $(\text{EtO})_2\text{P}$ and 23.9 g. $\text{BrCH}(\text{CO}_2\text{Et})_2$ 3 hrs. on a steam bath gave 17 g. $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$, b.p. 160-1°, 1.4420, 1.1660; similarly $\text{ClCH}(\text{CO}_2\text{Et})_2$ and $(\text{EtO})_2\text{P}$ after 3 hrs. on a steam bath gave the same product, $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$, b.p. 160-1°, 1.4410, 1.1644; reaction of 10 g. $(\text{EtO})_2\text{POCl}$ with Na deriv. from 1.3 g. Na and 9.2 g. $\text{CH}_2(\text{CO}_2\text{Et})_2$ in Et_2O gave after 10 hrs. refluxing 5 g. $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$, b.p. 159-60°, n_D²⁰ 1.4458. This (1.4 g.) and 2 g. $\text{CO}(\text{NH}_2)_2$ as above gave 0.46 g. $(\text{EtO})_2\text{P}(\text{O})\text{CH}$

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A. N. Pudovik & T. M. Moshkina

(CONH)₂CO, m. 97°; the phosphonomalonate from an alternate route gave the same product, m. 98°. To Na deriv. from 2 g. Na and 10 g. CH₃Ac₂ was added 15 g. (EtO)₂POCl in Et₂O and after refluxing 12 hrs. the filtrate gave 5.3 g. (EtO)₂P(O)CHAc₂, b_p 161-2°, n_D²⁰ 1.4328. Refluxing 2 g. of this with 3 g. CO(NH)₂ in dioxane and dry EtONa 10 hrs., dissolving the ppt. in H₂O, acidifying with HCl and

concg. gave 0.4 g. (EtO)₂P(O)C(CMe)₂NH.CO.N.CMe, m. 115-17° (EtOH). XVIII. Reaction of incomplete esters of acids of phosphorus with α,β -unsaturated cyclic ketones and cyclohexenyl acetate. A. N. Pudovik and I. V. Kononova. *Ibid.* 1617-21. Addn. of (RO)₂POH or (RO)₂PSH to 2-cyclohexenone and its methylated analogs occurs readily after addn. of catalytic amts. of RONa; after termination of the exothermic reaction, the mixts. were neutralized with AcOH and distd., yielding the following esters: di-Et 3-oxocyclohexylphosphonate, 54%, b_p 170°, n_D²⁰ 1.2840, d₄ 1.1210; di-Me ester, 48%, b_p 160°, 1.4723, 1.2131; di-Et 3-oxocyclohexylthiophosphonate, 57%, b_p 182°, 1.4998, 1.1207; di-Me 3-oxo-2-methylcyclohexylphosphonate, 68%, b_p 162°, m. 98°; di-Et ester, 50%, b_p 166°, 1.4812, 1.1007; di-Et 3-oxo-2-methylcyclohexylthiophosphonate, 60%, b_p 165°, 1.4936, 1.1099; di-Me 3-oxo-1-methylcyclohexylphosphonate, 47%, b_p 162°, 1.4721, 1.1801; di-Et ester, 54%, b_p 167°, 1.4653, 1.1130; di-Et 3-oxo-1-methylcyclohexylthiophosphonate, 53%, b_p 172°, 1.4950, 1.1182; di-Et 3-oxo-2,5-dimethylcyclohexylphosphonate, 68%, b_p 163°, 1.4810, 1.0810; di-Me ester, 60%, b_p 165°, 1.4750, 1.1499; di-Et 3-oxo-2,5-dimethylcyclohexylthiophosphonate, 68%, b_p 173°, 1.4921, 1.0940; di-Bu 3-oxo-2,5-dimethylcyclohexylphosphonate, 59%, b_p 196°, 1.4580, 1.0189; di-Et 3-oxo-2,5,5-trimethylcyclohexylphosphonate, 60%, b_p 167°, 1.4641,

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A.N. Pudovik + T.M. Moskvin

1.0710. Addn. of satd. EtONa-EtOH dropwise to 10.5 g. $(\text{EtO})_2\text{POH}$ and 10.5 g. 1-cyclohexenyl acetate gave a very exothermic reaction which resulted, after cooling and acidification, in isolation of 5 g. cyclohexanone and 13 g. $\text{MeC}(\text{OAc})(\text{PO}(\text{OEt}))_2$ (I), b: 174-5.5°, d₄ 1.1511, n_D 1.4308; the latter product formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate. To 19 g. $\text{AcP}(\text{O}(\text{OEt}))_2$ and 15 g. $(\text{EtO})_2\text{POH}$ was added dropwise EtONa-EtOH and after the strongly exothermic reaction there formed 20 g. I, b: 180°, d₄ 1.1535, n_D 1.4300; I heated with BzCl in PhNMe_2 1 hr. at 60° was benzoylated to the extent of but 5.8%. Reaction of 6.3 g. 1-cyclohexenyl acetate with 7 g. $(\text{EtO})_2\text{PSH}$ in the presence of EtONa as above gave 3 g. cyclohexanone and 9.8 g. product, b: 169°, 1.1421, 1.4710, identified as $\text{MeC}(\text{OAc})(\text{PS}(\text{OEt}))_2$. The latter, b: 168-70°, 1.1410, 1.4710, also formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate. G. M. F.

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~~PUDVIK, A.N.~~; KOROZANOV, I.V.

New method for the synthesis of phosphinic and thiophosphinic acids.
Part 28: Reaction of incomplete phosphorous acid esters with
 α, β -unsaturated cyclic ketones and cyclohexenol acetate. Zhur.
ob.khim. 27 no.6:1617-1621 Je '57. (1957:16:7)

1. Kazanskiy gosudarstvennyy universitet.
(Phosphorous acid) (Cyclohexenol) (Ketones)

PUDOVIK, A. N.

Distrs 4E4j/4B20(j)

Anomalous reaction of α -halo ketones with esters of phosphorous acid. V. Reactions of halogen derivatives of methyl ketone and acetophenone with triethyl phosphite. A. N. Pudovik and L. G. Biktimirova (State Univ., Moscow). *Zhur. Obshch. Khim.* 27; 1708-12 (1957); cf. C.A. 50, 84884; 51, 18276. Haloketones having the halogen on a secondary C atom are more prone to the anomalous course of reaction with $(RO)_3P$ than halo ketones with halogen on the primary C atom. To 28.4 g. $MeCOCHClMe$ preheated to 90-100° was added 43.4 g. $(EtO)_3P$ and the mixt. gradually heated to 120° giving $EtCl$ and 35.3 g. $(EtO)_3P(O)OCMe:CHMe$ (I), b_p 110-115°, d_4^{20} 1.0598, n_D^{20} 1.4274; this heated with $EtONa-EtOH$ gave $MeEtCO$ and $(EtO)_3PO$; ozonolysis of the unsatd. ester gave AcH . Heating 49.8 g. $MeCOCHBrMe$ and 58.6 g. $(EtO)_3P$ in dry Et_2O gave after 2.5 hrs. refluxing 36 g. I, b_p 111.6-12°, 1.0578, 1.4272, and 5 g. $AcCHMeP(O)(OEt)_2$ (II), b_p 123-5°, d_4^{20} 1.0598. If the phosphite was added to the bromo ketone preheated to 110° and the mixt. heated 4 hrs. at 130-40° there was formed 37.9 g. I and 8.8 g. II. Heating I or II at 100° in H_2O , followed by periodic titrations, showed that I is sapond. more rapidly than II; in 20 hrs. 39.8% I was hydrolyzed, while only 14% II was attacked. To 20 g. $(EtO)_3P$ preheated to 120° was added 14.6 g. 2-bromocyclohexanone yielding 3.1 g. $(EtO)_3POH$ and 13.4 g. di-Et cyclohexenyl phosphate, b_p 144°, 1.1033, 1.4518; the same products formed on addn. of bromocyclohexanone to refluxing $(EtO)_3P$. Heating the ester with $EtONa-EtOH$ gave cyclohexanone and $(EtO)_3PO$, thus confirming the structure of the former. Addn. of 38.5 g. $(EtO)_3P$ to 49 g. $MeCOCHBrMe$ at 20-30° gave on distn. some $EtBr$ and

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PUDOVIK, A. N.; BIKTIMIROVA, L. G.

22.8 g. $(EtO)_2P(O)OCMe:CB_2Me$, b.p., 147-8° (some decomposition), 1.3481, 1.4655; passage of Cl into this ester in CCl_4 with ice cooling gave $(EtO)_2P(O)OCMeClCB_2Me$, b.p. 164-5°, 1.4677, 1.4760. Addn. of 22.7 g. $(EtO)_2P$ to 55.4 g. $BrCH_2COCHBr_2$ at 60° gave 7.1 g. $(EtO)_2P(O)OCMe:CB_2$, b.p., 145-8°, 1.6340, 1.4935 (with much decomposition). Addn. of 44 g. $(EtO)_2P$ to 50 g. $PhCOCHCl_2$ at 20-30° gave 71 g. $(EtO)_2P(O)OCPh:CHCl$, b.p., 139-40°, 1.2353, 1.5170, which chlorinated in CCl_4 with ice cooling to $(EtO)_2P(O)OCPhClCHCl$, b.p. 162-3°, 1.3487, 1.5149. Addn. of 39 g. $(EtO)_2P$ to 47.8 g. $PhCOCCl_2$ at 20-30° gave 53.8 g. $(EtO)_2P(O)OCPh:CCH$, b.p. 145-6°, 1.8945, 1.5200. $(EtO)_2P$ reacted with haloketones. On heating dichloro- and dibromobenzylideneacetone, 3,4-dichloro-2-hexanone, and 3,4-dichloro-4-methyl-2-pentanone to 100-50°, the products could not be distilled or isolated owing to decomposition and tar formation.

G. M. Kozolapoff

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PUDOVIK, A-N.

Distr: 4E4j/4E2c(j)/4E3d

V Anomalous reaction of α -halo halides with esters of phosphorous acid. VI Reaction of esters of phosphorous acid with halides of halosubstituted carboxylic acids. A. N. Pudovik and L. G. Biktimirova (State Univ., Kazan), *Zhur. Obshchei Khim.* 27, 2104-8 (1957); *Ch. Z.N.* 52, 3714c. —To $(RO)_3P$ was added the desired $RCOCl$ in which R is a halogen-bearing radical. The reactions were exothermic, requiring cooling. After termination of evolution of alkyl halide, the product were distd. Reaction of $(MeO)_3P$ with $ClCH_2COCl$, with heating 0.5 hr. at 100° gave 84% product identified as $(MeO)_2P(O)OC(CH_3)P(O)(OMe)_2$, b_p 141° , d_4 1.3214, n_D^{20} 1.4420; similar reaction with $(EtO)_3P$ gave the *tetra-Et* analog, 86.4%, b_p $125-6^\circ$, 1.1827, 1.4396. The same reaction run in Et_2O gave a low yield. Ozonolysis of the products in CCl_4 gave CH_2O , thus confirming the structure. $(MeO)_3P$ and $Me_2CBrCOBr$ similarly gave 92.3% product, identified as $Me_2C: C[PO(OMe)_2]OP(O)(OMe)_2$, b_p $131-2^\circ$, 1.2756, 1.4680, while $(EtO)_3P$ gave 90% corresponding *tetra-Et* ester, b_p $134-5^\circ$, 1.1602, 1.4503. $(MeO)_3P$ and CCl_3COCl at below 30° gave 78.3% $CCl_3: C[PO(OMe)_2]OP(O)(OMe)_2$, b_p $134-5^\circ$, 1.4901, 1.4770, while the $(EtO)_3P$ reaction gave 78.6% *tetra-Et* ester, b_p $132-3^\circ$, 1.3219, 1.4000. If the last reaction is run in Et_2O , there was obtained the above *tetra-Et* ester and a somewhat greater amt. of $CCl_3COP(O)(OEt)_2$, b_p 95° , 1.3916, 1.4632, which is evidently the intermediate in the formation of the di-phosphorus esters. The phosphonate is formed also if the phosphite is used in less than the theoretical amt. for the reaction with the acyl halide. Reaction of $(EtO)_3P$ with $MeCHBrCOBr$ at 100° (final temp.) gave 78.6% $MeCH: C[PO(OEt)_2]OP(O)(OEt)_2$, b_p $128-9^\circ$, 1.1690, 1.4450. Thus, halosubstituted acyl halides react with phosphites predominantly by the anomalous route. G. M. Kosolapoff

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PUDOVIK, A.N.

Glorious anniversary on the eightieth birthday and fiftieth
anniversary of scientific activity of Academician A.E. Arbuzov.
Zhur. ob. khim. 27 no.9:2312-2328 S '57. (MIRA 11:3)
(Arbuzov, A.E. 1877-)

Pudovik, A. N.

4 Addition of alcohols to isoprene oxide. A. N. Pudovik and S. G. Denislamova (State Univ., Kazan, Kazan. Khim. 27, 2363-7(1957); cf. Petrov, C.A. 43, 8157c; Kadesch, C.A. 40, 1450). To 185 ml. dry MeOH was added 0.15 ml. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ followed, with cooling, by 34 g. 1,2-epoxy-2-methyl-3-butene (I) and after 4 hrs. on a steam bath the mixt. gave 13 g. 2-methoxy-2-methyl-3-buten-1-ol (II), b_p 75-8°, n_D^{20} 1.4390, d_4^{20} 0.9457, and 4.5 g. mixed products, b_p 98-170°. II with BzCl and PhNMe_2 in 1 hr. at 60° gave 36% *Bz* deriv. I (34 g.) added to 1 g. Na in 200 ml. dry MeOH and heated 10 hrs. on a steam bath gave 15.6 g. 1-methoxy-2-methyl-3-buten-2-ol, b_p 62.5-3°, n_D^{20} 1.4285, d_4^{20} 0.9193, and 1.7 g. II. Similarly $\text{BF}_3 \cdot \text{Et}_2\text{O}$, I, and EtOH gave 2-ethoxy-2-methyl-3-buten-1-ol, b_p 52.3-3.3°, 1.4380, 0.9227, while a reaction with EtOH contg. some Na gave but small amt. of this product, and much 2-methyl-1-ethoxy-3-buten-2-ol, b_p 45-6°, 1.4720, 0.8971. Similarly, I and BuOH in presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ gave mainly 2-butoxy-2-methyl-3-buten-1-ol (III), b_p 80-1°, 1.4390, 0.9030, and a product of further addn., $\text{C}_{11}\text{H}_{20}\text{O}_2$, b_p 124-5°, 1.4550, 0.9360; I and BuOH contg. a little Na gave mostly 1-butoxy-2-methyl-3-buten-2-ol, b_p 69.5-70.5°, 1.4303, 0.8777, and a little III. I and iso-BuOH with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ gave 2-isobutoxy-2-methyl-3-buten-1-ol, b_p 67-8°, 1.4380, 0.9001, while iso-BuOH-iso-BuONa treatment gave mainly 1-isobutoxy-2-methyl-3-buten-2-ol, b_p 58.5-9°, 1.4270, 0.8730, and a little of the above isomer. Allyl alc. and I in presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ gave mainly 2-allyloxy-2-methyl-3-buten-1-ol, b_p 77-8°, 1.4530, 0.9392, while reaction with ROH-RONa gave mainly 1-allyloxy-2-methyl-3-buten-2-ol, b_p 68.5-9.5°, 1.4455, 0.9164, and a little of the above isomer. G. M. K.

Distr: 4E2c(j)/4E4j/4E3d

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PUDOVIK, A.N.; SHCHELKINA, L.P.; BASHIROVA, L.A.

Substitution reaction of phosphoacetic ester and phosphoacetone.
Zhur. ob. khim. 27 no.9:2367-2371 S '57. (MIRA 11:3)

1. Kazanskiy gosudarstvennyy universitet.
(Acetic acid) (Acetone)

PUDOVIK, A.N.; SHERGINA, I.V.

Allyl regrouping. Part 19: The reaction of magnesium organic compounds and sodium diethylphosphorate with isomeric isoprene hydrochloride and methoxychloroisohexanes. Zhur.ob.khim. 27 no.10: 2750-2755 0 '57. (MIRA 11:4)

1. Kazanskiy gosudarstvennyy universitet.
(Magnesium—Organic compounds)
(Isoprene) (Hexane)

PU DVP K, A. N.

Dealkylation of isomeric tributyl phosphates by hydrogen chloride A. N. Fudovik (State Univ., Kazan), *Zh. Obshch. Khim.* 27, 2765-66 (1957); *Chem. Abstr.* 52, 3228g; Abramov and Karp, *C.A.* 49, 13887c. It is now shown that (RO)₃P are intermediate products in the reaction of PCl₅ with isomeric butenols; the initial dealkylation of these occurs along the lines of Arbuzov rearrangement by the attack of HCl. Further attack by HCl may pursue S_N1 or S_N2 routes. Since (RO)₃POH are attacked by dry HCl at -10° only very slowly if the radicals in the esters are primary and secondary, the rapid dealkylation of diisobutyl and diisobutenyl esters may be explained by direct action of HCl on the quinquivalent form of the ester through 4-center reaction at the PO group with electron supply provided by induction of alkyl groups aiding the reaction. Crotyl alc. (84.8 g.), 109 g. PhNMe₂, and 41.3 g. PCl₅ in Et₂O gave 45.5 g. (MeCH:CHCH₂O)₂P, b₁ 98-9°, d₄ 0.9767, n_D 1.4680; this (10 g.) treated with dry HCl at -10° gave 6.5 g. mixed chlorobutenes (86% 1-chloro-2-butene and 14% 2-chloro-3-butene) and 3.2 g. H₃PO₄. Addn. of 37 g. PCl₅ to 50 g. crotyl alc. at -15° gave after 0.5 hr. stirring and quenching in ice 59.5 g. mixed chlorobutenes of the same compn. as above. Similarly, PCl₅ and MeCH(OH)CH:CH₂ gave the same mixt. of chlorides. PCl₅ with BuOH under these conditions gave 84% (BuO)₃PHO, while allyl alc. gave 42% (CH₂:CHCH₂O)₃PHO (on distn. the residue tends to ex-

Distr: 4E4j/4E2c(j)/4E3d

4
2 may
3

1/2

A. N. Pudovik

plode violently if heated unduly). Passage of dry HCl into (BuO)₃P at -10° and stirring 0.5 hr. gave 1 mole BuCl and (BuO)₂PHO. Similarly, (CH₃:CHCH₂O)₃P and HCl gave allyl chloride and (RO)₂PHO, b_p 97-8°, n_D²⁰ 1.4430, with much residue. HCl with (CH₃:CHCHMeO)₃P gave H₃PO₄ and mixed butanyl chlorides (50-3% 1-chloro-2-butene and 47-50% 2-chloro-3-butene). Keeping (RO)₃P in Et₂O in the presence of dry HCl at room temp. and following the reaction by periodic analysis for labile Cl showed that in 8 days the Bu ester lost 0.96, allyl ester lost 1.7, crotyl ester lost 2.3, and methallyl ester lost 2.2 ester groups.

G. M. Kosolapoff

4
2 may
3

am JH 2/2

AUTHORS: Pudovik, A. N., Konovalova, I. V.

79-28-5-16/69

TITLE: A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids (Novyy metod sinteza efirov fosfinovykh i tiofosfinovykh kislot) XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic- and Sorbic Acid, as Well as to the 3,5-Heptadienone-2 (XXIX. Prisoyedineniye dialkilfosforistykh kislot k efiram vinilakrilovoy, sorbinovoy kislot i 3,5-heptadiyenonu-2)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1208 - 1211 (USSR)

ABSTRACT: In continuation of earlier papers (Reference 1) the authors describe the results of the addition reactions of dimethylphosphorous and diethylphosphorous acids to the esters of the β -vinylakrylic- and sorbic acids, to 3,5-heptadienone-2, and to the diethylester of butadienephosphinic acid. Alkali alcoholates were used as catalysts in these reactions. All reactions take a vigorous course and are accompanied by a considerable heat effect. Products of the addition of one or two molecules were obtained as result of the addition of diethylphosphorous acid (in excess) to the ethylester of β -vinylakrylic

Card 1/3

79-28-5-16/69

A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids. XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic- and Sorbic Acid, as Well as to the 3,5-Heptadienone-2

acid, namely: the ethylesters of 4-(diethylphosphonium)butene-2-carboxylic acid (formula I of scheme 1) and 2,4-di-(diethylphosphonium)butanecarboxylic acid (II). The structure of (I) was hardened by ozonization and decomposition of the ozonides. The binding of diethylphosphorous acid to the ethylsorbinate also leads to the formation of two products (III and IV of scheme 2). Product (III) contains a double bond and represents a product of the addition of a molecule of diethylphosphorous acid. From the obtained ozonization results could be concluded that (III) represents mainly a γ,δ -product of the addition, which contains the forms α,β - or α,δ -(or both together). Product (IV) does not contain a double bond and represents an addition product of two molecules of diethylphosphorous acid to 3,5-ethylsorbinate. In the case of the addition of diethylphosphorous acid to 3,5-heptadienone-2, compound (V) with a double bond resulted. By ozonization

Card 2/3

79-28-5-16/69

A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids. XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic-and Sorbic Acid, as Well as to the 3,5-Heptadienone-2

and further treatment of the ozonides this formula was proved.
There are 2 references, which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: May 3, 1957

Card 3/3

AUTHORS: Pudovik, A. N., Biktimirova. L. G. SOV/79-28-6-11/63

TITLE: The Anomalous Reaction of α -Halogen Ketones With Esters of Phosphorous Acid (Anomal'naya reaktsiya α -galoidketonov s efirami fosforistoy kisloty) VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine Derivatives of β -Diketones (VII. Reaktsii efirov fosforistoy kisloty s khlorproizvodnymi β -diketonov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1496-1500 (USSR)

ABSTRACT: In the present paper the authors investigated the reactions of the chlorine- and dichlorine-substituted compounds of acetyl-benzoyl-acetone, dibenzoylmethane and dimedone with various phosphites. As was to be predicted from earlier results obtained unsaturated esters of phosphoric acid occurred as intermediate or final products in all these reactions. The reactions of chloro- and dichloroacetylacetone with trimethyl- and tri-n-butylphosphite take place completely anomalously: in yields of 60 - 80 % (1-methylbutene-1-on-3-yl)-dialkyl-, or (1-methyl-2-chlorobutene-1-on-3-yl)-dialkyl-ester of phosphoric acid respectively were obtained. (See

Card 1/3

30779-28-6-11/63

The Anomalous Reaction of α -Halogen Ketones With Esters of Phosphorous Acid. VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine Derivatives of β -Diketones

formulae I - IV of the table). The presence of double bonds in these compounds was proved by bromination according to Mak-Ilineyu. In the case of careful saponification of compound (I) of the table acetylacetone was obtained. It is of interest that after two months this compound turned brown at room temperature and smelled like acetylacetone. In fact 10 % of the latter could be separated in the distillation, the residual representing the unchanged product. In carrying out the reactions of chlorobenzoylacetone with trimethyl- and triethylphosphite (yield 70 - 80 %) the (1-phenylbutene-1-on-3-yl)-dimethyl- and (1-phenylbutene-1-on-3-yl)-diethyl-ester of phosphoric acid were obtained (formula V and VI of the table). Also in this case the double bonds were determined by bromination and on storing this compound a small amount of benzoylacetone crystallized out, too. Thus all these reactions take an anomalous course and not one according to the regrouping as mentioned by Arbuzov (Ref 1). Some of these unsaturated esters of phosphoric acid, especially those with

Card 2/3

SOV/ 79-28-6-11/63

The Anomalous Reaction of α -Halogen Ketones With Esters of Phosphorous Acid. VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine Derivatives of β -Diketones

the phenyl- and cyclohexene radical split up on heating under the formation of a β -dicarbonyl compound. There are 3 figures, 1 table, and 4 references, 3 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet
(Kazan' State University)

SUBMITTED: May 3, 1957

1. Ketones--Chemical reactions 2. Phosphoric acids--Chemical reactions

Card 3/3

PUDOVIK, A.N.; CHEBOTAROVA, E.G.

Anomalous reaction of phosphites with α -halogenketones. Part 8:
Reactions of mixed phosphites with chloro and dichloro acetone.
Zhur.ob.khim. 28 no.9:2492-2496 S '58. (MIRA 11:11)

1. Kazanskiy gosudarstvennyy universitet.
(Acetone) (Phosphites)

FUDOVIK, A.N.; ALADZHEVA, I.M.

Addition of ammonia and amines to isoprene oxide. Zhur.ob.khim.
28 no.9:2497-2500 S '58. (MIRA 11:11)

1. Kazanskiy gosudarstvennyy universitet.
(Ammonia) (Amines) (Isoprene)

5(3)

AUTHORS: Kukhtin, V. A., Iudovik, A. N. (Zagan') SOV/74-26-1-5/5

TITLE: Several New Types of Arbuzov Rearrangements
(nekotoryye novyye vidy peregruppirovki Arbuzova)

REFERENCE: Dopekhi khimii, 1959, Vol 28, Nr 1, pp 96-116 (USSR)

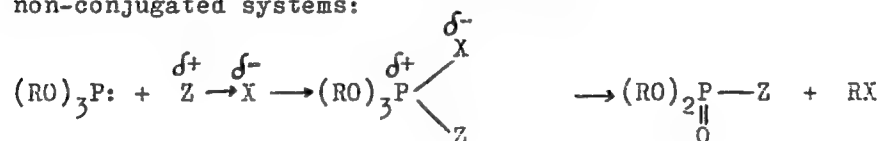
ABSTRACT: The reaction listed in the scientific publications as the rearrangement of Arbuzov was discovered in 1905 by A. Ye. Arbuzov. At present it represents one of the most important methods for synthesizing esters of phosphinic acids and their derivatives. The authors of this paper give a review of the most recent research work on this reaction and on broadening its application. In summary it may be said that the chemistry of trivalent phosphorous has entered a new phase of development. The basic type of Arbuzov rearrangement has been found to be characteristic of a whole new series of reactions of phosphites with various reagents. The current understanding of the Arbuzov reaction, which has been concerned only with the effect of alkyl halogens on the esters of trivalent phosphorous (Refs 86, 87), must be expanded on the basis of existent experimental material. The transformation of esters of trivalent phosphorous to derivatives of pentavalent

Card 1/4

Several New Types of Arbuzov Rearrangements

SOV/74-28-1-5/5

phosphorous, which takes place using saturated as well as - unsaturated electrophilic reagents with and without halogen atoms, should be considered a part of the Arbuzov rearrangement, since it is accompanied by the formation of a new P-El bond (El= C, N, O, S, and others). The nature of the rearrangement consists in the primary attack on the especially electrophilic part of the molecule by the nucleophilic phosphorous atom to form, usually, an intermediate form. This form then splits off the ester radical of the phosphite through the effect of the especially electronegative part of the associated reagent to form the endproduct, in which the P=O bond has formed. There are at least three basic types of Arbuzov rearrangements: 1. Rearrangement under the effect of non-conjugated systems:

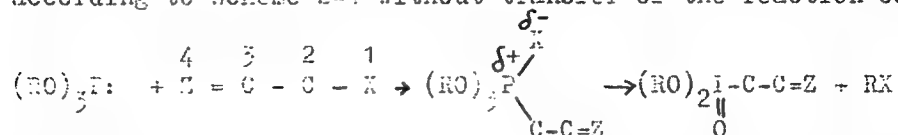


Card 2/4

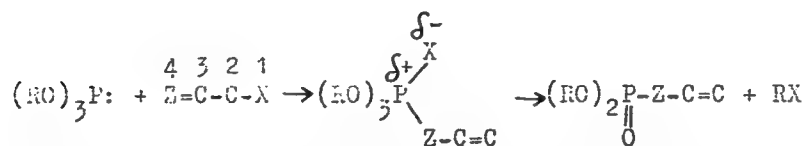
Several New Types of Arbuzov Rearrangements

SOV/74-28-1-5/5

2. Rearrangement under the effect of σ , π -conjugated systems. This type can occur in the following directions. a) Reaction according to scheme 2-1 without transfer of the reaction center:



b) Reaction according to scheme 4-1 or with transfer of the reaction center:

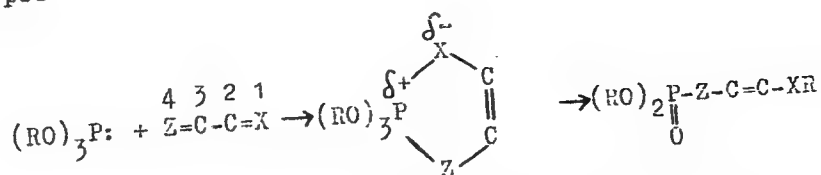


3. Rearrangement involving π , π -conjugated systems apparently occurs always by scheme 4-1 with transfer of the reaction center:

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Several New Types of Arbuzov Rearrangements

SOV/74-26-1-5/5



These three basic types apparently cannot include all the various cases of this reaction. Complicated electron systems with a mixed conjugation (e.g. halogen acrylates, lactones, and several others) exhibit specific behavior in the reaction. Reagents which tend to form free radicals can be included in the Arbuzov rearrangement under certain conditions, according to the radical-chain mechanism, which differs from all the others mentioned above. Esters of trivalent phosphorous have not only the tendency to undergo the Arbuzov rearrangement, but they can also undergo numerous other reactions. Further research work on the rearrangement of Arbuzov promises to yield new and interesting results. There are 87 references, 57 of which are Soviet.

Card 4/4

USCOMM-DC-60841

AUTHORS: Pudovik, A. N., Platonova, R. N. SOV/79-29-2-31/71

TITLE: On the Reaction of Phosgene and Oxalyl Chloride With Esters of Phosphorous Acid (O reaktsii fosgena i khloristogo oksalila s efirami fosforistoy kisloty)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 507-510 (USSR)

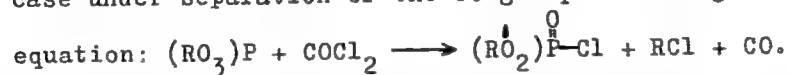
ABSTRACT: In connection with previous investigations concerning reactions of phosphites with halogen anhydrides of α -halogen-substituted carboxylic acids it was a matter of course that the authors would carry out the reactions of phosphites with halogen anhydrides of dibasic acids. The results they obtained in the reactions of complete phosphites with phosgene were in contrast to those described by M. I. Kabachnik and P. A. Rossiyskaya (Ref 6). On the reaction of phosgene with triethyl phosphite the authors obtained the chloric anhydride (IV), which, together with ethyl alcohol in the presence of pyridine or sodium ethylate, permitted substitution of the ethoxy group for chlorine, while ester (V) was formed simultaneously. According to the data obtained by Kabachnik's and Rossiyskaya's investigation, the ethyl ester of diethyl phosphonoformic acid

Card 1/3

On the Reaction of Phosgene and Oxalyl Chloride
With Esters of Phosphorous Acid

SOV/79-29-2-31/71

$((C_2H_5O)_2\overset{O}{P}-COOC_2H_5)$ ought to be formed. This ester obtained by A. Ye. Arbuzov (Ref 7) by action (VI) of chlorocarbonic ester on triethyl phosphite was not identical with compound (VI). For this reason, the authors repeated its synthesis according to reference 7. The constants of the products synthesized are listed in table 1. It results from them that compound (V) does not agree with (VI) but represents a triethyl phosphate. After further experiments of identification, i.e., due to the reaction of phosgene with the methyl, ethyl, and butyl ester of phosphorous acid, and 2) after the synthesis of some chloric anhydrides of dialkyl phosphoric acids by the action of chlorine on dialkyl phosphorous acids (Table 2), in the course of which the reaction products were identical in both cases and represented chloric anhydrides of dialkyl phosphoric acid, the following results were obtained: the reactions of phosgene with complete esters of phosphorous acid take place in any case under separation of the CO group according to this



Card 2/3

On the Reaction of Phosgene and Oxalyl Chloride
With Esters of Phosphorous Acid

SOV/79-29-2-31/71

The reaction of the chloric anhydride of oxalic acid with trimethyl and triethyl phosphite also takes place in the same way, yet the respective yields are smaller (last-mentioned Scheme). There are 2 tables and 9 references, 7 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: December 26, 1957

Card 3/3

SOV/79-29-4-38/77

5(3)

AUTHORS:

Nikitina, V. I., Pudovik, A. N.

TITLE:

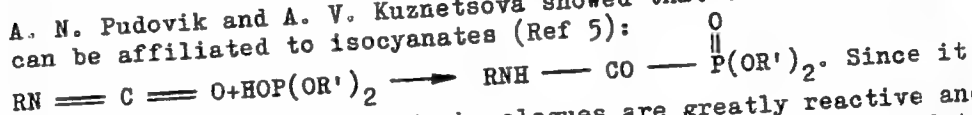
A New Method for the Synthesis of Phosphinates and Thiophosphinates (Novyy metod sinteza efirov fosfinovykh i tiofosfinovykh kislot). XXX. On the Reaction of Dialkyl Phosphorous and Dialkyl Thiophosphorous Acids With Ketene (XXX. O vzaimodeystvii dialkilfosforistykh i dialkiltiofosforistykh kislot s ketenom)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1219-1222 (USSR)

ABSTRACT:

A. N. Pudovik and A. V. Kuznetsova showed that the above acids can be affiliated to isocyanates (Ref 5):



Since it is known that ketene and its homologues are greatly reactive and are easily affiliated to various compounds, the authors tried to cause ketene to react as well. When carrying out the reactions of dialkyl phosphorous acids with ketene they found that these reactions require a catalyst, and that it is necessary to add to the reaction mixture a small quantity of pyridine or sulfuric acid in order to initiate the reaction. During the transformation of ketene with dimethyl-, diethyl-, dibutyl-, and di-isobutyl

Card 1/3

A New Method for the Synthesis of Phosphinates and Thiophosphinates. XXX. On the
Reaction of Dialkyl Phosphorous and Dialkyl Thiophosphorous Acids With
Ketene SOV/79-29-4-38/77

phosphorous acids two products form in either case: dialkyl acetophosphinates, and products of their further transformation with ketene (Scheme 2). Generally the quantity of both products is 75-80%; the acetophosphinate yield is only a fraction of the acetoxyvinylphosphinate yield. The structure of acetophosphinates was determined according to reference 6, that of acetoxyvinylphosphinates by means of the double bond. Formaldehyde results from the ozonation of the acetate of dimethyloxyvinylphosphinate. The second stage of the reaction was carried out separately. By the transformation of ethylacetophosphinate with ketene in the presence of pyridine the diethylacetoxyvinylphosphinate was obtained. The data obtained, as well as those obtained by the analyses and molecular refraction, prove the structure of the acetates of oxyvinylphosphinates. The constants of acetophosphinates and acetoxyvinylphosphinates are contained in the table (Products 1-8). The reactions of ketene with dialkylthiophosphorous acids take place in a similar way, but the acetoxyvinylthiophosphinate yields are smaller in these reactions than in those mentioned

Card 2/3

5(3)

AUTHORS:

Pudovik, A. N., Sitdikova, F. N. SOV/20-125-4-38/74

TITLE:

Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone (Prisoyedineniye nepolnykh efirov kislot fosfora k nitroizoamilenu i etil-vinilsul'fonu)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 4, pp 826-828 (USSR)

ABSTRACT:

The authors continue their work (Ref) in the field of the addition of esters of various phosphorus containing acids etc to other compounds. It was of interest to extend the field of application of the mentioned reactions to the unsaturated nitro compounds and unsaturated nitrosulfones. This would facilitate a simple and convenient method of synthesis of nitrophosphinic- and sulfophosphinic esters which normally is either difficult or impossible (Refs 2-4). The catalysts were alcoholates of alkali metals without solvent. It was very easy to add dimethyl- and diethyl phosphoric acid to nitroisoamylene. In this connection a considerable amount of heat was produced. The reaction products are weakly smelling distillable liquids of a slightly yellow color. The addition of the ethyl ester of phosphonoacetic acid to nitroisoamylene

Card 1/3

SOV/20-125-4-38/74

Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone

is more difficult. It requires considerable amounts of alcoholate and temperatures of 100-110° during several hours. A rather long induction period precedes the reaction. Table 1 shows the constants of the products obtained. Nitroisoamylene polymerizes only weakly in this connection. The experiments dealing with the addition of diethyl- and dimethyl thiophosphorus acid to furyl nitroethylene and ω -nitrostyrene in the presence of alcoholates of alkali metals as well as in the presence of organic bases, further the carrying out of the reaction in solutions in all cases led to a more rapid polymerization than it was the case with the addition reaction, in spite of the use of catalysts milder (piperidine and triethylamine) than alcoholates. It was not possible to isolate the addition products, and after a several hours heating at 80-90° only the initial products were isolated. It is well-known that certain nucleophilic reagents easily add to the double bond of unsaturated sulfones, in which connection various derivatives of saturated sulfones form. The addition products are distillable liquids or crystalline colorless substances, with a weak smell (Table 2). The reactions described

Card 2/3

SOV/20-125-4-38/74

Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone

in the present paper were carried out according to the method of reference 1. The reagents were used in equimolar amounts (1/20 - 1/30 mole). Thus, it was proved that the dialkyl phosphorous- and dialkyl thiophosphorous acids as well as the acid esters of alkylphosphinic acids in the presence of an alkali catalyst are capable of adding to the double bond of the α -unsaturated nitro compounds and sulfones. There are 2 tables and 4 references, 3 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet im. V. I. Ul'yanova-Lenina
(Kazan' State University imeni V. I. Ul'yanov-Lenin)

PRESENTED: December 19, 1958, by B. A. Arbuzov, Academician

SUBMITTED: November 28, 1958

Card 3/3

S/079/60/030/007/014/020
B001/B067

AUTHORS: Pudovik, A. N., Konovalova, I. V.

TITLE: A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. Addition of Dialkyl Thiophosphorous Acids and Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7,
pp. 2348 - 2352

TEXT: In continuation of their earlier paper (Ref. 1) the authors studied the addition reactions of dialkyl thiophosphorous acids and acid esters of alkyl- and aryl phosphinic acids. They proceeded from diethyl-, di-n-propyl-, diisopropyl-, di-n-butyl thiophosphorous acid, from methyl-, ethyl-, butyl ester of ethyl phosphinic acid, and from methyl-, ethyl ester of phenyl phosphinic acid. The addition was made to hydrocarbons of the aliphatic series, from heptene-1 to undecene-1, and to cyclohexene. The reactions took place under irradiation of the reaction mixtures with a mercury-quartz lamp or under heating in the presence of

Card. 1/3

A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. Addition of Dialkyl Thiophosphorous Acids and Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated Hydrocarbons

S/079/60/030/007/014/020
B001/B067

benzoyl peroxide. In both cases, the same alkyl thiophosphinates, dialkyl phosphinates, and the esters of alkyl-phenyl phosphinic acids were obtained with yields of 40-65%. A scheme of the reaction course is given. The reactions (1-3) show the initiation process and the growth of the chain, as well as the formation of the addition product. Reaction (4) causes the formation of the polymer residue at the expense of further telomerization. At an equivalent ratio of the initial reagents the polymeric residue is formed in a quantity of 10-15% of the addition product. It was shown that the dialkyl thiophosphorous acids and the acid esters of phosphinic acids add to olefins even without catalysts; a prolonged heating at 135-140° is sufficient. The addition products which were obtained by irradiation on the one hand and by the presence of benzoyl peroxide on the other are identical. The reaction rate in the case of cyclohexene was characterized by a change in concentration of the acid in the reaction mixture. It was shown that with increasing radical the phosphinate yield is gradually and slowly reduced (Fig. 1).

Card 2/3

A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. S/079/60/030/007/014/020
Addition of Dialkyl Thiophosphorous Acids and B001/B067
Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated Hydrocarbons

The alkyl thiophosphinates, dialkyl phosphinates, and alkyl-phenyl phosphinates are characterized in Tables 1 and 2. The acids obtained from them by saponification are given in Table 3. On the basis of the experimental results the authors arrived at the conclusion that the addition of dialkyl thiophosphorous acids to olefins in both cases does not proceed according to the Markovnikov rule but to the radical mechanism (Scheme 2). There are 2 figures, 3 tables, and 2 Soviet references.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: July 6, 1959

Card 3/3

PUDOVIK, A.N.; MURATOVA, A.A.; KONNOVA, T.I.; FEOKTISTOVA, T.; LEVKOVA,
L.N.

Reactions of esters of alkyl phosphonic acids with halogen-
containing compounds. Zhur.ob.khim. 30 no.8:2624-2630 Ag
'60. (MIRA 13:8)

1. Kazanskiy gosudarstvenny universitet.
(Phosphonic acid)

PUDOVIN, A.N.; KONOVALOVA, I.V.

New method of synthesizing esters of phosphinic and thiophosphinic acids. Part 35: Addition of phosphorus pentochloride to diene hydrocarbons and of partial esters of phosphorus acids to butadiene-phosphinic esters. Zhur.ob.khim. 31 no.4:1693-1699 My '61.
(MIRA 14:5)

1. Kazanskiy gosudarstvennyy universitet.
(Phosphinic acid)

PUDOVIK, A.N.; ALADZHEVA, I.M.

Esters of ethyleneglycoldiphosphorous acid. Zhur.ob.khim. 31 no.6:
2052-2057 Je '61. (MIRA 14:6)

1. Kazanskiy gosudarstvennyy universitet.
(Phosphorous acid)

PUDOVIK, A.N.; MEDVEDEVA, G.P.; KOCHETKOVA, V.I.

Reactions of phosphorous acid cyclic esters with α -halo ketones.
Zhur.ob.khim. 31 no.8:2650-2656 Ag '61. (MIRA 14:8)

1. Kazanskiy gosudarstvennyy universitet.
(Phosphorous acid) (Ketones)

25367

S/079/61/031/008/005/009
D215/D304

158150

AUTHORS: Pudovik, A.N., Konovalova, I.V., and Durova, O.S.

TITLE: A new synthesis method of phosphinic and thiophosphinic acids and esters. XXXIII. Synthesis of unsaturated phosphonic and thiophosphonic acids esters

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 8, 1961, 2656-2661

TEXT: This study is a continuation of previous investigations, in which it was found that derivatives of unsaturated acids of phosphorus can be obtained by adding to their incomplete esters acetylene compounds, activated with some electron repellent groups in presence of an alkaline catalyst. In this work it is shown that this method may be applied to acetylene compounds directly in conditions stimulating the mechanism of free radicals chain addition. As incomplete esters of phosphorus acids, the following compounds were used: dimethyl and diethyl-phosphorous acid esters, diethyl and di-isopropylthiophosphorous acid esters, and ethyl and isopropyl ethyl phosphonic acid esters. The addition of these

Card 1/5

25367

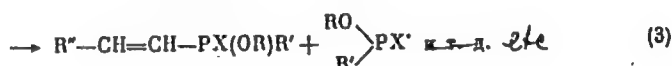
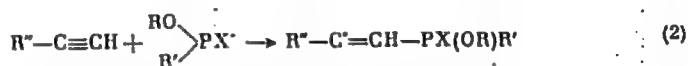
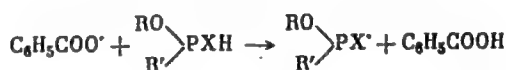
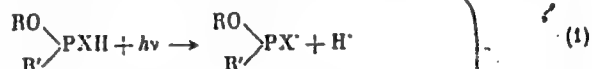
S/079/61/031/008/005/009
D215/D304

A new synthesis method ...

esters to heptyne-1 and octyne-1 was carried out by irradiating the reaction mixture with ultra-violet light or in presence of benzoylperoxide. The chain reaction is illustrated by the following reactions.

(1), (1a), (2) and (3) correspond to initiation chain-growing and the formation of the addition product; N(4) - formation of the polymerization product. In both synthesis reactions (irradiation or benzoylperoxide), the same products - esters of alkenyl phosphoric or alkenylthiophosphonic acids were obtained,

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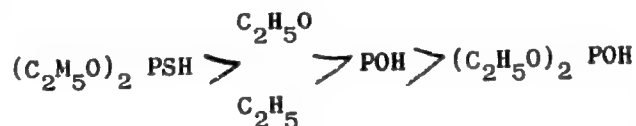
25367

S/079/61/031/008/005/009
D215/D304

A new synthesis method...

[Abstractor's note: British nomenclature of phosphorus organic compounds is used: "onic" for quinquivalent and "inic" for tervalent P] with a yield of 25-50%, the esters being mobile, colorless liquids, sparingly soluble in water, highly soluble in organic solvents. Their characteristics are given in tabulated form. The structure of addition products was proved by the oxidation of the diethyl ester of hephenylthiophosphonic acid with KMnO_4 , when n - caproic acid was obtained.

The authors investigated the addition reaction velocity of heptyne-1 to acidic ethylesters of phosphorous, thiophosphorous and ethylphosphinic acids; they found that the velocity of reaction decreased in the following series:



The obtained results prove that the investigated reactions take place through free radicals chain mechanism and against Markownikoff's rule

Card 3/5

25367

S/079/61/031/008/005/009
D215/D304

A new synthesis method...

[Abstractor's note: His name is written thus in technical literature].
The velocity of addition reactions of the above-mentioned esters with heptane-1, heptyne-1 and phenylacetylene decreases as follows: heptane-1 heptyne-1 phenyl-acetylene. The velocity of reactions are given graphically. It is seen that the velocity of reaction with benzoylperoxide is quite similar to that which is carried out by irradiation and that the addition reaction with phenylacetylene is much slower than others. The yield of the last reaction was very low, due to the resinification of reagents. The obtained product: diethylester of β -phenylvinylthiophosphonic acid was described by previous investigators, but its constants given by them differ from those found by the authors; the previously published constants were erroneous because MR based on the given data is markedly different from the calculated one. The authors carried out the synthesis of di-phosphonic derivatives by adding di-ethylphosphorous and di-ethylthiophosphorous acids to the diethylester of heptenylthiophosphonic acid, in the presence of sodium ethoxide, the reaction being an ionic one. The reaction products are thick, colorless liquids,

Card 4/5

25367

S/079/61/031/008/005/009
D215/D304

A new synthesis method...

almost insoluble in water, soluble in organic solvents. There are 1 table, 2 figures and 18 references: 14 Soviet-bloc and 4 non-Soviet-bloc. The references to the 4 most recent English-language publications read as follows: U.S.A. Patents AN 2611784, 2622096, Ch.A. 47, 9355, 9344 (1953); C.S. Marvel, T.C. Wright, Y. Polym, Sci. 8, 255 (1952); K. Leedman, R.N. Haszeldine, Y. Chem. Soc. 1634, (1954); T. Heilbron, E.R. Jones, H. Bander, L.C. Gross, Y. Chem. Soc. 604, (1949).

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan State University)

SUBMITTED: July 25, 1960

Card 5/5

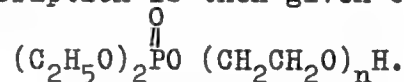
S/019/61/031/012/006/011
D258/D301

AUTHORS: Pudovik, A. N., and Moshkina, T. M.

TITLE: Polyethylene glycols and some of their derivatives

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4028-4033

TEXT: The authors synthesized several polyethylene glycols of the general formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ and the esterification products of these with either one or two molecules of $(\text{C}_2\text{H}_5\text{O})_2\text{POCl}$ and ClCH_2COCl (separately). The products were assumed to be useful as plasticizers in producing materials for motion pictures, as surfactants and as tanning agents. The molecular weights of the lower glycols were determined by cryoscopy. The glycols are soluble in alcohol, benzene, dioxane and water; their solubility in ether decreases with increasing molecular weight. A description is then given of the preparation of monophosphate esters



Card 1/2

Polyethylene glycols and ...

S/079/61/031/012/006/011
D258/D301

The principal characteristics of the synthesized polyethylene glycols (I) and their monophosphates (II), diphosphates (III), monochloroacetates (IV) and dichloroacetates (V) are given in tabulated form. There are 1 figure, 3 tables and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The reference to the English-language publication reads as follows: R. Forgyce, H. Lovell and H. Hibbert, J. Am. Chem. Soc., 61, 1905, (1939). ✓

ASSOCIATION: Kazanskiy filial nauchno-isslyedovatel'skogo kino-fotoinstituta (Kazan Branch of the Scientific Research Moving Picture Photography Institute)

SUBMITTED: December 26, 1960

Card 2/2

5 3630

31195
S/079/61/031/012/009/011
D204/D301

AUTHORS: Pudovik, A. N., and Krupnov, G. P.

TITLE: A new method of synthesizing phosphinic and thiophosphinic esters. XXXVI. Synthesis of phosphinic acid derivatives containing cyclic radicals in the ester group

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4053-4055

TEXT: Compounds of the general formulae $(RO)_2 \overset{O}{\underset{|}{P}} CH_2 CH(R')X$ (I), where $R = C_6H_{11}^-$, $C_6H_5CH_2^-$, $R' = -H$, $-CH_3$, $X = -CN$, $-COOCH_3$, $-COOC_4H_9$ and $(RO)_2 \overset{O}{\underset{|}{P}} CH(C_6H_5)NHC_6H_4X$ (II), where $R = C_6H_{11}^-$, $C_6H_5^-$, $C_6H_5CH_2^-$, $X = p-CH_3$, $-H$, $p-NO_2$ were prepared in a search for new plasticizers for cellulose esters and other polymers. The ge-
Card 1/3

31195

S/079/61/031/012/009/011

D204/D301

A new method of synthesizing ...

neral method of preparation consisted of adding esters of dicyclohexyl, dibenzyl and diphenyl phosphorous acids to unsaturated, electrophilic compounds, in the presence of a catalyst. Na alcoholate in absolute alcohol was added dropwise to an equimolecular mixture of the appropriate phosphorous ester and either an ester or nitrile of an unsaturated carboxylic acid or a Schiff's base, with constant stirring, keeping the temperature below 50-90°C. The reaction mixture was then heated for 1 - 2 hours on a steam bath. The products were purified either by distillation (ordinary or high-vacuum), or by repeated washing with water to remove the catalyst, and drying. The yields were 13.6 - 68% in the case of (I) and 61 - 88% in the case of (II). Distillation of the reaction products was difficult owing to a tendency towards charring and decomposition, but comparable purity could be achieved by the washing method. Esters (I) were colorless, involatile liquids insoluble in water but soluble in a number of organic solvents; aminophosphinic esters (II) were crystalline substances, insoluble in water but soluble in alcohol. Physical constants of both types of products are tabulated. There are 2 tables and 3 references: 2 Soviet-bloc

Card 2/3

31195

S/079/61/031/012/009/011
D204/D301

A new method of synthesizing ...

and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: Atherton, Koward and A. Todd, J. Chem. Soc. (1948), 1182.

ASSOCIATION: Kazanskiy filial vsesoyuznogo nauchno-issledovatel'skogo kinofotoinstituta (Kazan Branch of the All-Union Scientific Research Institute of Motion Picture Photography)

SUBMITTED: December 26, 1960

X

Card 3/3

29016

S/020/61/140/004/017/023

B106/B110

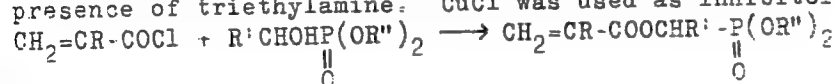
15 815D

AUTHORS: Pudovik, A. N., Kashevarova, E. I., and Rudnev, Yu. P.

TITLE: Phosphorus-containing acrylic and methacrylic esters

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 841-843

TEXT: Polymers and copolymers of acrylic and methacrylic esters containing sulfur, fluorine, tin, lead, silicon, mercury, etc. often have particular properties: high hardness and heat resistance, good adhesion to glass and metal, low permeability to X-rays, low combustibility, etc. In this connection, a method was developed for the synthesis of acrylic and methacrylic esters containing phosphorus in the alcohol component. Some properties of these esters were studied. The synthesis is based on the reaction of acid chlorides of acrylic and methacrylic acids with hydroxy-alkyl phosphinic esters (molar ratio 1 : 1) in ether solution in the presence of triethylamine. CuCl was used as inhibitor.



Card 1/6 ~

29016

S/O20/61/140/004/C17/C23

B:06/B110

Phosphorus-containing acrylic ...

(R = H or CH₃; R' = H or CH₃; R'' = CH₃, C₂H₅ .) Reactions proceed smoothly in most cases, esters form with yields of 60-70%. The α-hydroxy-alkyl phosphinic esters used as initial substances were prepared by reacting formaldehyde and acetaldehyde with dialkyl phosphorous acids in the presence of sodium alcoholate, acryl and methacryl chlorides were obtained from acids by reaction with phosphorus trichloride. The characteristics of the acrylic and methacrylic esters synthesized are shown in Table 1. All these compounds are easily soluble in methanol, ethanol, ether, acetone, benzene, and carbon tetrachloride. Moreover, esters containing methyl and ethyl radicals in the phosphono group are soluble in water. When the α-(dimethyl phosphono)-ethyl methacrylic ester is polymerized in the presence of 0.3 mole% benzoyl peroxide (9 hr at 80°C), a solid transparent polymer formed which swelled strongly in water, alcohol, benzene, acetone, and carbon tetrachloride. The polymer burns with sooty flame, but does not keep burning by itself. The polymer obtained by polymerization of α-(diethyl phosphono)-ethyl methacrylic ester in the presence of 0.5 mole% benzoyl peroxide (30 hr at 100°C) is a soft, transparent, plastic mass readily soluble in methanol, ethanol, and acetone. It is precipitated by petroleum ether from solutions in benzene.

Card 2/63

29016

S/020/61/140/004/017/023

B106/B110

Phosphorus-containing acrylic

and acetone. Methyl methacrylate and α -(dimethyl phosphono)-ethyl methacrylic ester (weight ratio 83 : 17) were copolymerized at 75°C for 1.5 hr. The copolymer obtained is a transparent and solid product soluble in acetone and benzene. A white, solid, nontransparent product containing 2.2% phosphorus was obtained after reprecipitating by dissolution in acetone precipitating with petroleum ether, and subsequent drying in vacuo. This copolymer burns with sooty flame and keeps burning when the flame has been removed. There are 1 table and 16 references: 11 Soviet and 5 non-Soviet. The three most recent references to English-language publications read as follows: G. Sumrell, I. Briskin, G. Ham, C. S. Shramm, J. Am. Chem. Soc., 81, 4308 (1959); C. S. Marvel, W. S. Anderson, Ind. and Eng. Chem., 47, 344 (1955); A. Saiton, E. Rochow, J. Org. Chem., 23, 116 (1958).

ASSOCIATION: Kazanskiy gosudarstvennyy universitet im. V. I. Ul'yanova-Lenina (Kazan' State University imeni V. I. Ul'yanov-Lenin)

PRESENTED: May 8, 1961, by B. A. Arbuzov, Academician

SUBMITTED May 5, 1961

Card 3/65

PUDOVIK, A.N.; MOSHKINA, T.M.

Polyethylene glycols and some of their derivatives. Zhur.
ob.khim. 31 no.12:4028-4033 D '61. (MIRA 15:2)

1. Kazanskiy filial Nauchno-issledovatel'skogo kinofotoinstituta.
(Glycols)

PUDOVIK, A.N.; KRUPNOV, G.P.

New method of synthesizing esters of phosphinic and thiophosphinic acids. Part 36: Synthesis of the derivatives of phosphinic acids with cyclic radicals in ester groups. Zhur. ob.khim. 31 no.12:4053-4055 D '61. (MIRA 15:2)

1. Kazanskiy filial Vsesoyuznogo nauchno-issledovatel'skogo kinofotoinstituta.

(Phosphinic acid)
(Phosphinitic acid)

PUDOVIK, A.N., KUZNETSOV, YE.V., MALICHENKO, B.F., GRISHINA, O.P.

The synthesis of various phosphorus-containing monomers.

Report presented at the 12th Conference on high molecular weight compounds,
devoted to monomers, Baku, 3-7 April 62

PUDOVIK, A.N.; FAYZULLIN, E.M.

Reactions of phosphorus acid chlorides with glycerol epichlorohydrin
and glycidol ethers. Zhur. ob. khim. 32 no.1:231-237 Ja '62.

(MIRA 15:2)

1. Kazanskiy gosudarstvennyy universitet.

(Phosphorus acids) (Glycerol) (Ether)

PUDOVIK, A.N.; KONOVALOVA, I.V.; ISHMAYEVA, E.A.

New method of synthesizing phosphinic and thiophosphinic acid esters.
Part 37: Addition of nucleophilic reagents to butadiene- and
methylbutadienephosphinic esters. Zhur. ob. khim. 32 no.1:237-241
Ja '62. (MIRA 15:2)

1. Kazanskiy gosudarstvennyy universitet.
(Phosphinic acid)

FUDOVIK, A.N.; KONOVALOVA, I.V.

Reactions of vinyl acetate with partial esters of phosphorus
acids. Zhur.ob.khim. 32 no.2:467-471 F '62. (MIRA 15:2)
(Vinyl acetate)
(Phosphorus acids)